Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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Continuum of Covalent to Intermolecular Bonding in the Halogen-Bonded Complexes of 1,4-Diazabicyclo[2.2.2]octane with Bromine-Containing Electrophiles

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A) UV-Vis and NMR measurements and their treatments

UV-Vis measurements were carried out in acetonitrile at 22 ^{o}C using quartz (1-mm or 2-mm path length) spectroscopic cells on a CARY 500 spectrophotometer. A Dewar equipped with a quartz lens was used for the measurements at +5 to -70 ^{o}C. The temperature was adjusted with an ethanol-liquid nitrogen bath (±0.5 K). The formation constants represent average values from 3-5 series of UV-Vis titration experiments. Each series typically included 8-10 data points. UV-Vis absorption values measured at two wavelengths were normally used in the calculations.

An addition of DABCO to the solutions of R-Br electrophiles in acetonitrile resulted in the appearance of absorption bands in the 200 - 400 nm range. Lowering the temperature resulted in (reversible) increase of these band, indicating that they are related to the formation of complex. UV-Vis spectral titration data (Figures S1-S6) and Job's plots (Figure S7) were consistent with the formation of 1:1 complex (although different stoichiometry of the complexes are generally possible due to the presence of multiple binding sites in both halogen-bond donors and acceptors). It confirms that 1:1 complexes (eq S1) were predominant under conditions of UV-Vis spectral measurements of equilibria constants in Table 1. [1]

Extinction coefficients ε for [R-Br, DABCO] complexes, and equilibrium constants of their formation in Table 1 were calculated via the Benesi-Hildebrand procedure and, additionally, via regression analysis:

$$CHX_3 + A^- \overset{K}{\rightleftharpoons} [CHX_3, A^-] \quad \text{(S1)}$$

The formation constant of the complex is expressed as

$$K = C_{com} / ((C^o_D - C_{com})(C^o_A - C_{com})) \quad \text{(S2)}$$

where C_{com} is the concentartion of the complex, and C^o_D and C^o_A are the initial concentrations of R-Br and DABCO, respectively. When $C^o_A >> C^o_D$, $C^o_A - C_{com} \approx C^o_A$. Therefore $K_{eff} = C_{com} /((C^o_D - C_{com})C^o_A))$. Thus,

$$K_{eff}(C^o_D - C_{com})C^o_A - C_{com} = 0 \quad \text{(S3)}$$

Or
$$C_{com} = K_{eff}C^o_D C^o_A /(K_{eff}C^o_D + 1) \quad \text{(S4)}$$

Taking into account that: $\Delta Abs = \varepsilon\, l\, C_{com}$, where ΔAbs is the absorbance of the complex at a certain wavelength (obtained by subtraction of the absorption of the components), and l is the length of the spectrophotometric cell, the latter can be rearranged as the Benesi-Hildebrand equation:

$$C^o_D /\Delta Abs = 1/(\varepsilon\, l) + \{1/ (K_{UV}^{eff}\ \varepsilon l)\} \times 1/[\ C^o_A] \quad \text{(S5)}$$

The Benesi-Hidenbrand treatments of the UV-Vis absorption data are illustrated below in Figures S1C-S6C. It should be noted that the Benesi-Hildebrand procedure provided reliable results only if one reactant is present in large excess and the complexation of the other reactant (in deficit) is in the 20-80% range. These conditions are difficult to satisfy for complexes with K < 1 or less and for complexes with K > 100. Thus, to verify the values of K and ε, we carried out a regression analysis of the UV-Vis data without assumptions made in the Benesi-Hildebrand method. In this case, eq S2 leads to:

$$C_{com} = (C^o_A + C^o_D + 1/K_{eff}) +/- (((C^o_A + C^o_D + 1/K_{eff})^2 - 4C^o_A\, C^o_D)^{0.5}\}/2 \quad \text{(S6)}$$

So, changes in the UV-Vis absorption intensity can be expressed as:

$$\Delta Abs = \varepsilon l \times C_{com} = \varepsilon l \times (C^o_A + C^o_D + 1/K_{eff}) - (((C^o_A + C^o_D + 1/K_{eff})^2 - 4C^o_A\, C^o_D)^{0.5}\}/2 \quad \text{(S7)}$$

The fitting of the results of the UV-Vis titrations to eqs S7 (with ε and K^f as the adjustable parameters) using OriginPro 2016 are illustrated in Figures S1D-S6D. They produced values of K and ε which were generally consistent with those obtained via the Benesi-Hildebrand treatment.

[1] This is probably related to the fact that these titrations were performed under the conditions of the excess of DABCO, while polarization of the halogen-bonded R-Br hindered bonding of another halogen-bond acceptor.Since substantial separation of bonding sites in DABCO makes bonding of two electrophiles essentially independent, 2:1 R-Br/DABCO complexes are probably formed if excess of R-Br electrophile is used.

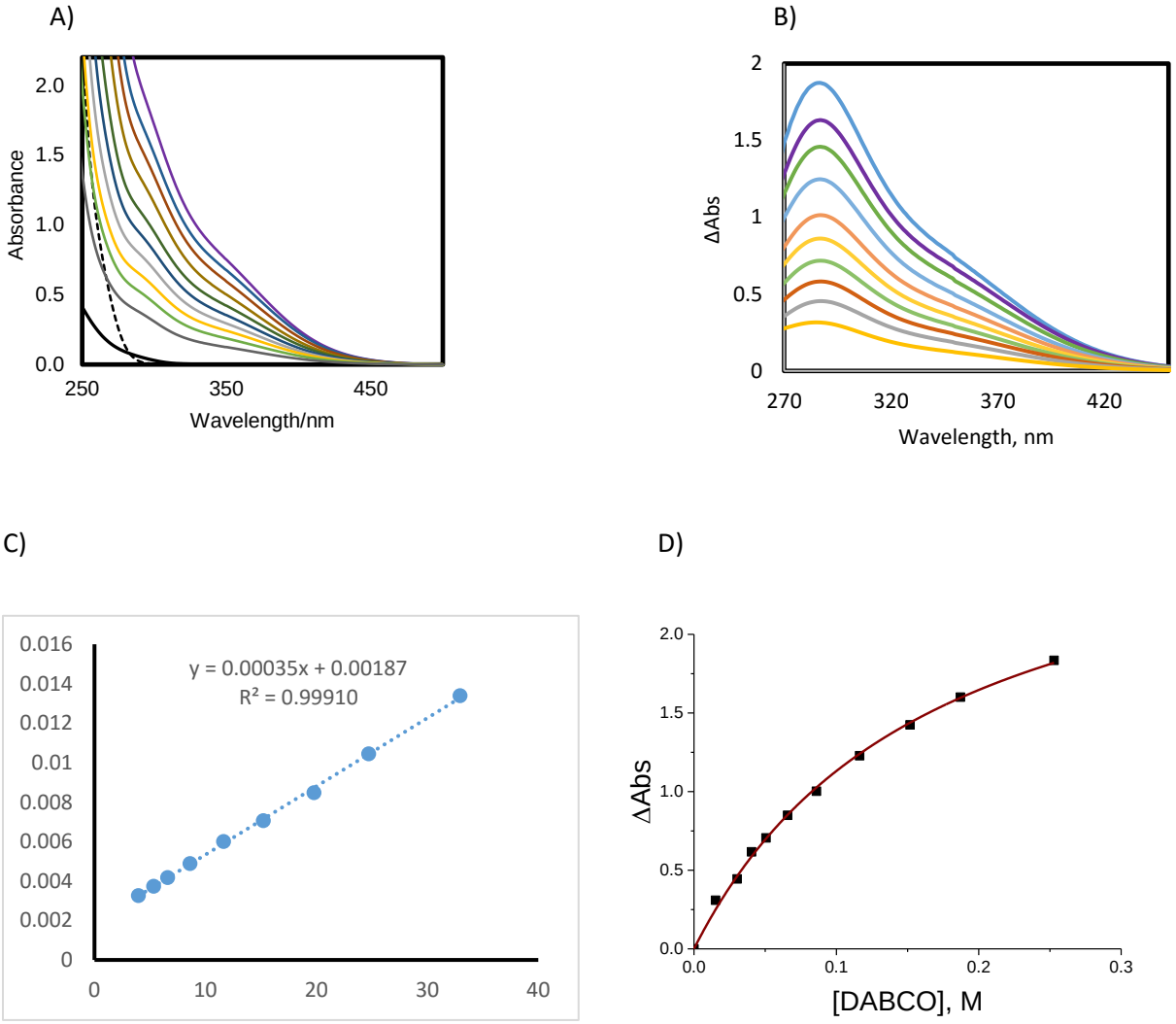


Figure S1. A) UV-Vis spectral changes upon addition of DABCO to a solution of CBr_3NO_2 in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Benesi-Hildebrand treatment of absorption data.

D) Results of the fitting of the spectral data (ΔAbs) to eq S7.

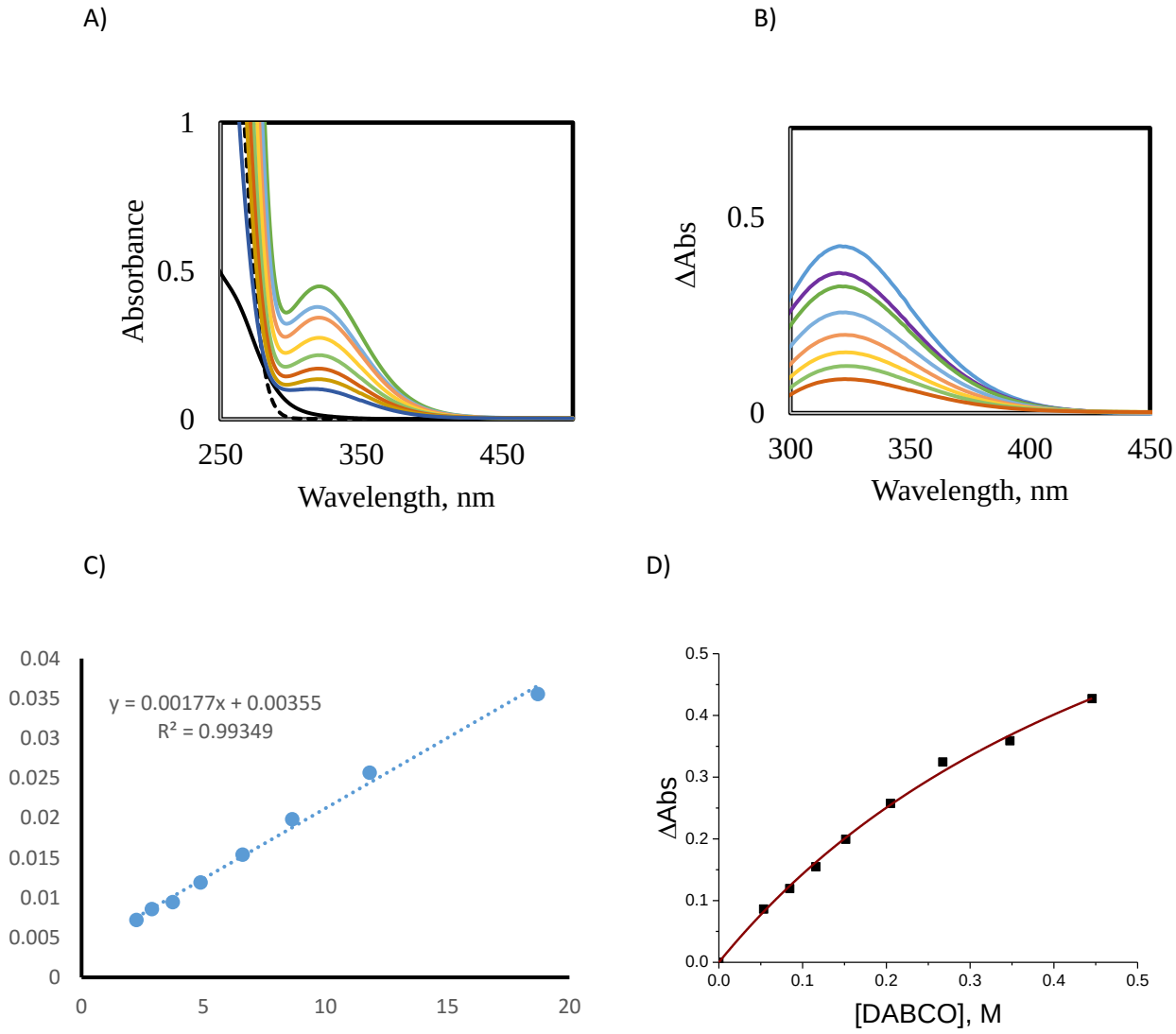


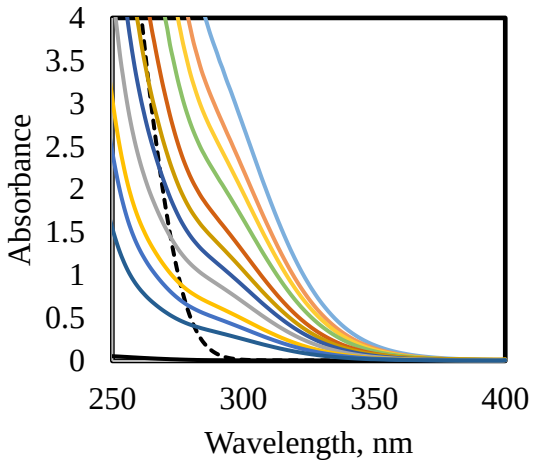
Figure S2. A) UV-Vis spectral changes upon addition of DABCO to a solution of CBr_3COCBr_3 in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Benesi-Hildebrand treatment of absorption data.

D) Results of the fitting of the spectral data (ΔAbs) to eq S7.

A)



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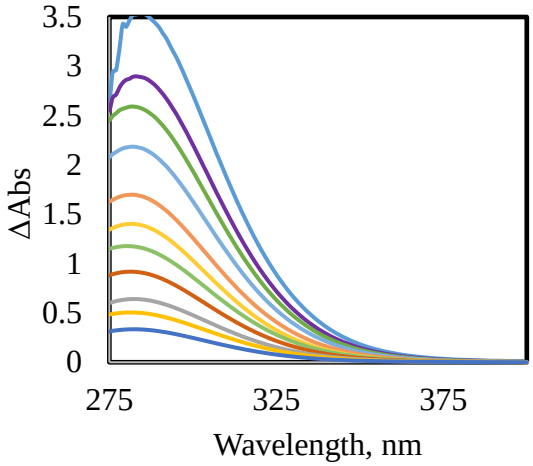

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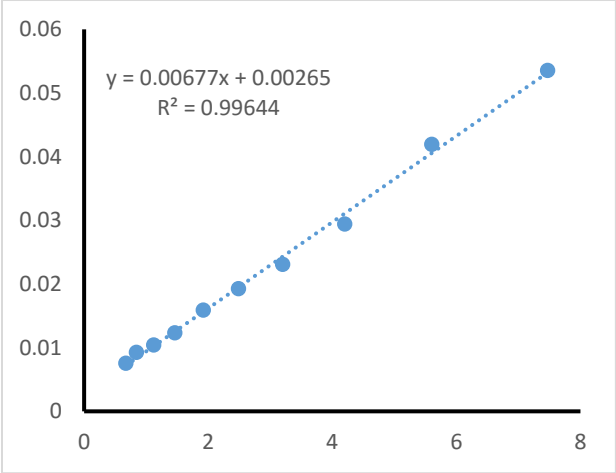


D)

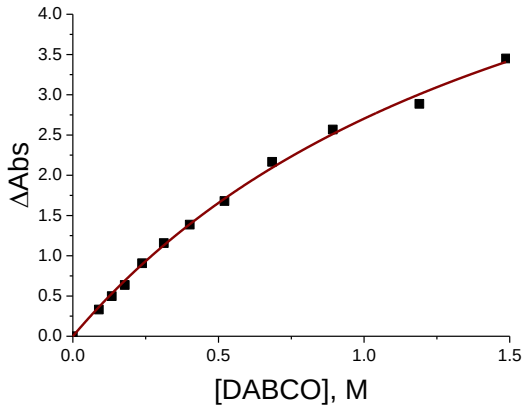


Figure S3. A) UV-Vis spectral changes upon addition of DABCO to a solution of $CBrCl_3$ in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Benesi-Hildebrand treatment of absorption data.

D) Results of the fitting of the spectral data (ΔAbs) to eq S7.

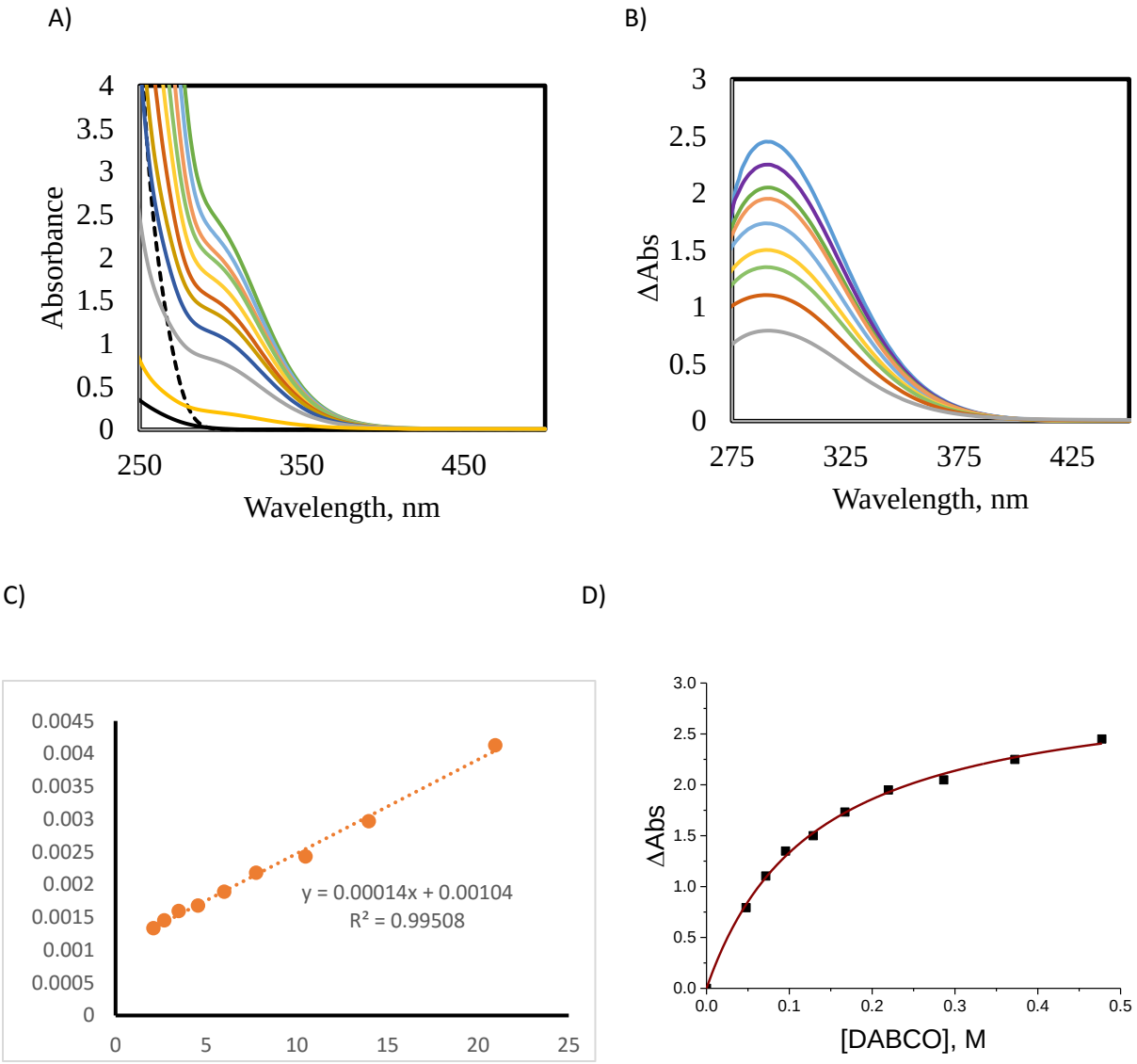


Figure S4. A) UV-Vis spectral changes upon addition of DABCO to the solution of CBr_3CN in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Benesi-Hildebrand treatment of absorption data.

D) Results of the fitting of the spectral data (ΔAbs) to eq S7.

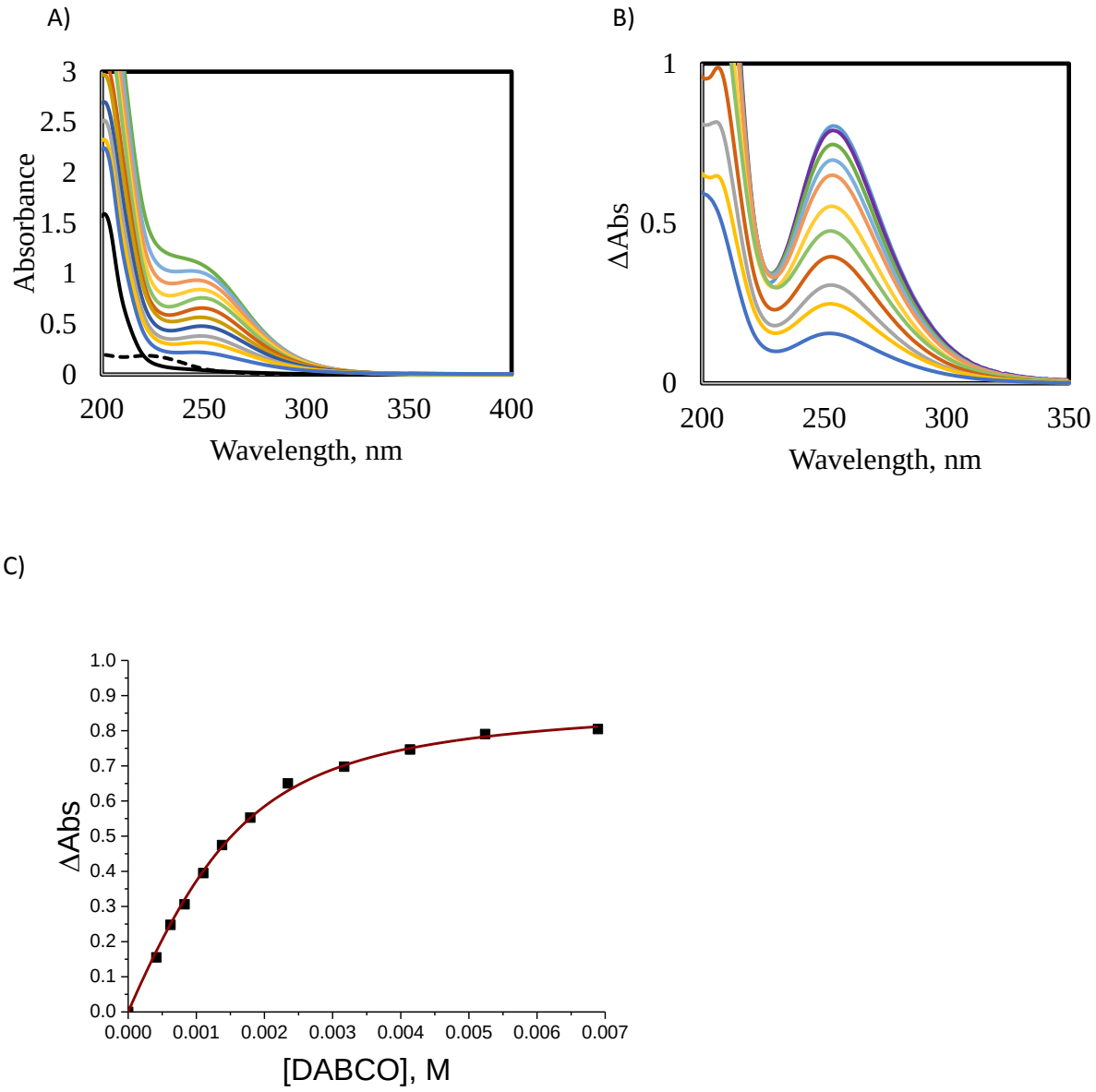


Figure S5. A) UV-Vis spectral changes upon addition of DABCO to a solution of CBr_3CN in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Results of the fitting of the spectral data (ΔAbs) to eq S7 (Benesi-Hildebrand treatment is not applicable in this case, since the concentrations of C_{DABCO} are comparable to that of $C_{R\text{-}Br}$.

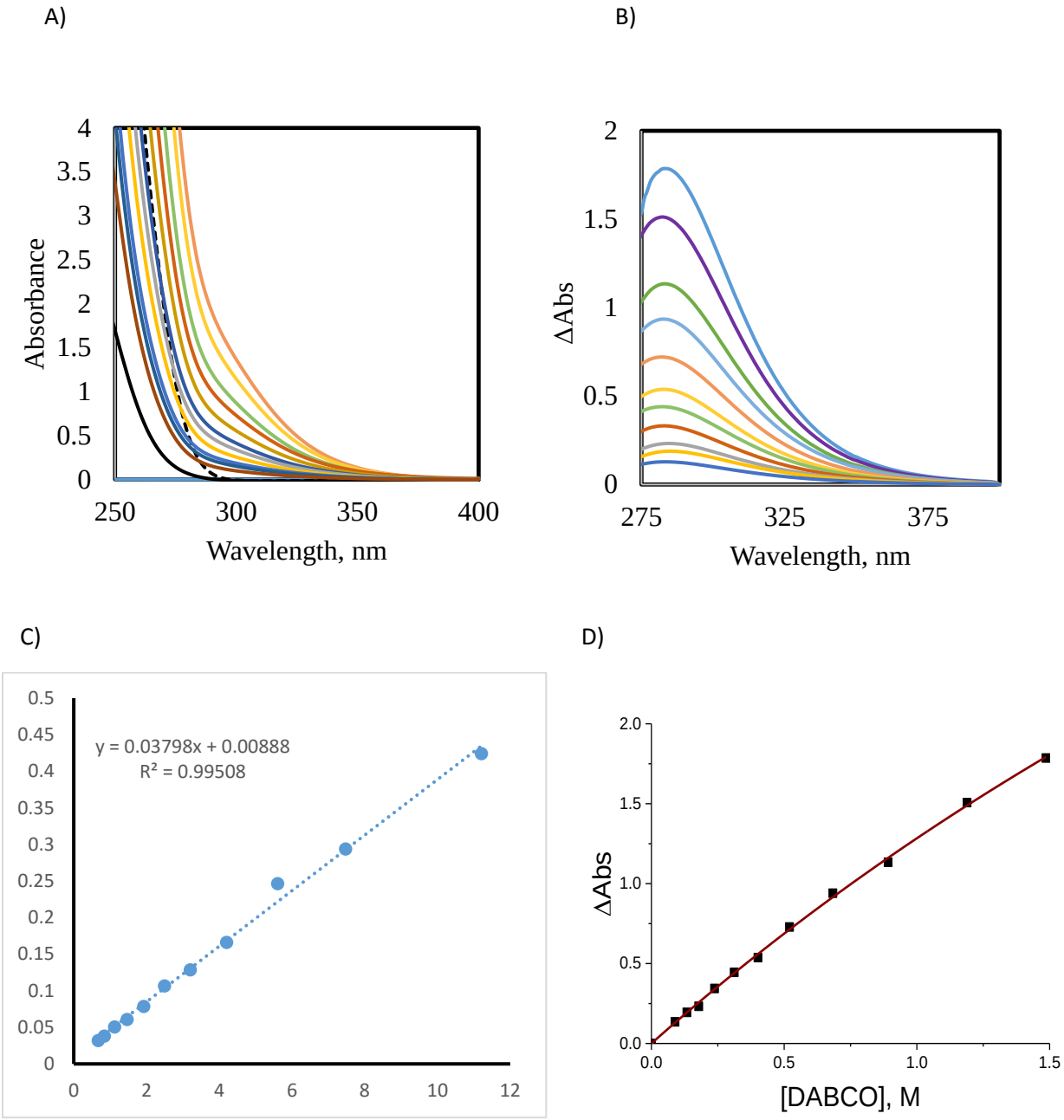


Figure S6. A) UV-Vis spectral changes upon addition of DABCO to a solution of $CHBr_3$ in acetonitrile. The solid and dashed black lines represent pure R-Br and pure DABCO solutions, respectively.

B) Differential absorption spectra obtained by subtraction of the absorption of components from the spectra of the mixtures representing absorption spectra of the [R-Br-DABCO] complex.

C) Benesi-Hildebrand treatment of absorption data.

D) Results of the fitting of the spectral data (ΔAbs) to eq S7.

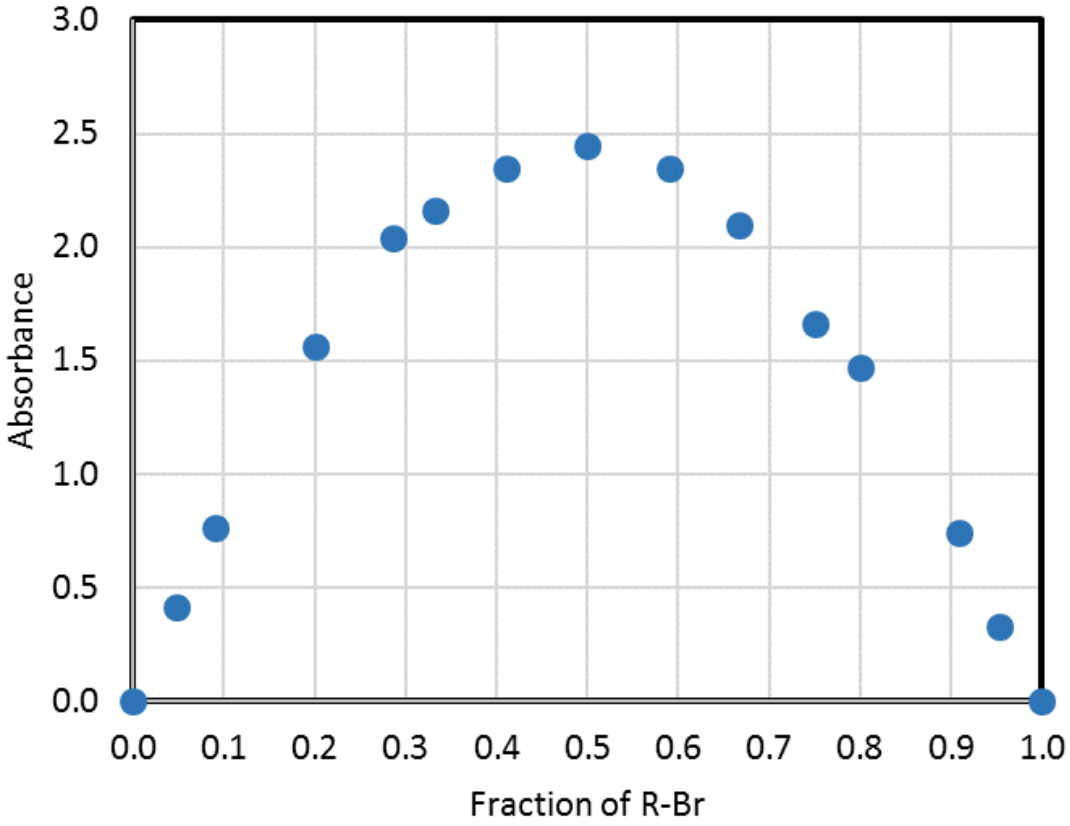


Figure S7. Jobs plot: dependence of the intensity absorption of the [R-Br, DABCO] complex (R-Br = CBr_3F) on the fraction of R-Br in the solutions showing peak at 1:1 ratio of reactants indicating formation of 1:1 complex.. Measurements were carried out in acetonitrile at λ = 310 nm, and the absorption values of complex were obtained by the subtraction of the absorption of components from the spectra of their mixtures. The sum of concentrations of components was constant (50 mM).

Single crystal growth and X-ray crystallographic analysis

Commercially available 1,4-diazabicyclo[2.2.2]octane (DABCO), carbon tetrabromide, bromoform, tribromofluoromethane, hexabromoacetone, N-bromosuccinimide, N-bromosaccharine, N-bromophtalimide were purified by recrystallization, sublimation or distillation under vacuo. Tribromonitromethane was synthesized by bromination of nitromethane, tribromoacetamide was prepared by reaction of hexabromoacetone with NH4OH, and tribromoacetonitrile was synthesized by dehydration of tribromoacetamide with P_2O_5 as described previously.[1]

Single-crystals of the halogen-bonded complexes for X-ray structural measurements were prepared by either slow evaporation or by slow cooling of solutions containing the R-Br electrophiles and DABCO. Single crystal of DABCO·CBr_3NO_2 were prepared from 112 mg (1.0 mmol) of DABCO and 298 mg (1.0 mmol) of CBr_3NO_2, dissolved in a minimum amount of chloroform and cooled slowly (in the thermoisolating box) to 2^o C in a refrigerator upon which yellow crystals suitable for X-ray analysis formed. Single crystals of complexes of DABCO with CBr_3F, $CHBr_3$, CBr_3CONH_2 and $CBrCl_3$ were prepared in a similar way. Colorless crystals which comprised [DABCO-Br-DABCO]$^+$ triads and sacharate anions were prepared by evaporations of a solution containing 25 mg (0.22 mmol) of DABCO and 60 mg (0.23 mmol) of N-bromosaccharine in acetonitrile at room temperature. Pale-yellow co-crystals of dibromine and DABCO were prepared by evaporation of the solutions containing a solution containing 50 mg (0.45 mmol) of DABCO and 75 mg (0.47 mmol) of dibromine in the dichloromethane/hexane (3:1) mixture.

Single crystal diffraction data were collected on one of two instruments. A single crystal of the DABCO-CBr_3NO_2 complex suitable for X-ray diffraction studies was mounted using a trace of mineral oil on a glass fiber and measured on a Bruker AXS Kappa APEX-II diffractometer equipped with a CCD area detector and an Oxford Cryosystems low temperature device using Cu Kα radiation (λ = 1.54178 Å) at 100(2) K. Crystals of the other complexes were mounted onto Mitegen micromesh mount using a trace of Fomblin oil and were transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, a single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at 100 K (for complexes with CBr_3F, $CHBr_3$, CBr_3CONH_2 and $CBrCl_3$) or 150 K ([DABCO-Br-DABCO]$^+$ ·$C_7H_4NO_3S^-$ and $(Br_2)_2$·DABCO). Data were collected, reflections were indexed and processed, and the files scaled using APEX3 [2] and corrected for absorption using Sadabs [3]. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [4] and refined by full matrix least squares against F^2 with all reflections using Shelxl2018 [5] and the graphical interface Shelxle [6]. If not specified otherwise H atoms attached to carbon

and nitrogen atoms and hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.88 Å for N-H, 0.95 Å for and aromatic C-H, 1.00 and 0.99 Å for aliphatic C-H and CH_2 moieties, respectively. U_{iso}(H) values were set to a multiple of U_{eq}(C) with 1.5 for CH_3, and 1.2 for C-H units, respectively. In CBr_3F· DABCO, two of four crystallographically DABCO molecules are disordered around inversion centers. Their geometries were restrained to be similar to that of another not disordered DABCO molecule, and U^{ij} components of ADPs were restrained to be similar to each other for atoms closer than 1.7 Å. In $CBrCl_3$·DABCO, The trichloro-bromo-methane molecules are disordered across a mirror plane and bromide atoms are 1:1 disordered with chloride atoms. Overlapping Br and Cl atoms were constrained to have identical ADPs, and all C-Cl bond distances were restrained to be similar. In DABCO-Br-DABCO^{+}·$C_7H_4NO_3S^{-}$, the oxo-benzoisothiazolide-dioxide fragment is 1:1 disordered around a two-fold axis. The benzene ring was restrained to resemble an ideal hexagon with C-H distances of 1.39 Å. The ethylene moieties of the DABCO unit were refined as disordered. The two disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 1.7 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.601(8) to 0.3999(8). The structure was refined as a 2-component inversion twin. Crystallographic, data collection and structure refinement details are listed in Table S1. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1843782 (CBr_3CONH_2·DABCO), 1843783 ($CHBr_3$·DABCO), 1843784 (CBr_3F·DABCO), 1843785 ((Br_2)$_2$·DABCO) 1843786 ($CBrCl_3$·DABCO), 1843787 (DABCO-Br-DABCO), 1843788 (CBr_3NO_2·DABCO) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1] S. V. Rosokha, C. L. Stern, J. T. Ritzert, *Chem. Eur. J.* **2013**, *19*, 8774–8788.

[2] Bruker (2016). Apex3 v2016.9-0, Saint V8.34A, SAINT V8.37A, Bruker AXS Inc.: Madison (WI), USA, 2013/2014.

[3] L. Krause, R, Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.

[4] a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA) b) Sheldrick GM. A short history of SHELX. *Acta Crystallogr A.* **2008**, *64(1)*, 112–122.

[5] a) Sheldrick GM. University of Göttingen, Germany, **2018**. b) Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71(1)*, 3–8.

[6] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44(6)*, 1281–1284.

Table S1. Crystallographic, data collection and structure refinement details

	CBr_3NO_2·DABCO	CBr_3F·DABCO	$CHBr_3$·DABCO	$CBrCl_3$·DABCO	CBr_3CONH_2·DABCO	[DABCO-Br-DABCO]$^+$	$(Br_2)_2$·DABCO
Chemical formula	$C_6H_{12}N_2$·Br_3CNO_2·$CHCl_3$	$C_6H_{12}N_2$·CBr_3F	$C_6H_{12}N_2$·$CHBr_3$	$C_6H_{12}N_2$·$CBrCl_3$	$C_6H_{12}N_2$·$C_2H_2Br_3NO$	$C_{12}H_{24}BrN_4$·$C_7H_4NO_3S$	$C_6H_{12}Br_4N_2$·CH_2Cl_2
M_r	529.29	382.92	364.92	310.45	407.95	486.42	516.74
Crystal system, space group	Orthorhombic, $Pna2_1$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/c$	Trigonal, $P3_221$	Monoclinic, $P2_1/m$
Temperature (K)	100	100	100	100	100	150	150
a, b, c (Å)	14.314 (2), 18.260 (3), 6.4262 (10)	6.5248 (4), 14.6823 (8), 19.4306 (13)	6.0754 (3), 15.7428 (9), 12.0401 (7)	5.8771 (3), 16.4201 (9), 11.9239 (6)	6.4062 (4), 20.4294(14) 9.5955 (6)	9.8558 (5), 9.8558 (5), 18.9035 (11)	7.7632 (3), 7.4280 (4), 12.8269 (6)
α, β, γ (°)	90, 90, 90	72.579 (2), 85.379 (2), 85.795 (2)	90, 101.8849(19) 90	90, 100.625 (2), 90	90, 92.369 (2), 90	90, 90, 90,	90, 98.7339 (15), 90
V (Å^3)	1679.6 (5)	1767.91 (19)	1126.88 (11)	1130.96 (10)	1254.74 (14	1590.22 (19)	731.09 (6)
Z	4	6	4	4	4	3	2
Device type	Bruker Kappa *APEXII* CCD	Bruker AXS D8 Quest CMOS diffractometer					
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	13.33	10.24	10.69	4.30	9.63	2.07	11.35
Density ρ_{calcd}	2.093	2.158	2.151	1.823	2.160	1.524	2.347
Crystal size (mm)	0.44 × 0.39 × 0.25	0.55 × 0.49 × 0.21	0.28 × 0.10 × 0.09	0.40 × 0.40 × 0.20	0.44 × 0.37 × 0.05	0.48 × 0.45 × 0.33	0.25 × 0.13 × 0.12
Absorption correction	multi-scan, *SADABS 2014*/5	multi-scan, *SADABS 2014*/5 or 2016/2					
T_{min}, T_{max}	0.045, 0.162	0.553, 0.747	0.462, 0.747	0.498, 0.747	0.455, 0.748	0.603, 0.747	0.386, 0.747
No. measured, independent and obsr [$I > 2\sigma(I)$] reflections	9754, 2603, 2596	42132, 5837, 10449	21426, 336, 3860	23547, 4405, 3439	12541, 3269, 2726	39226, 5144, 4167	36166, 2979, 2527
R_{int}	0.050	0.044	0.038	0.039	0.071	0.038	0.055
θ values (°)	θ_{max} = 65.1, θ_{min} = 4.8	θ_{max} = 36.5, θ_{min} = 2.8	θ_{max} = 36.4, θ_{min} = 3.1	θ_{max} = 33.1, θ_{min} = 3.0	θ_{max} = 29.6, θ_{min} = 2.9	θ_{max} = 36.4, θ_{min} = 3.2	θ_{max} = 33.2, θ_{min} = 3.2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.077, 1.11	0.047, 0.071, 1.05	0.033, 0.051, 1.03	0.038, 0.063, 1.12	0.049, 0.138, 1.08	0.027, 0.066, 1.05	0.024, 0.058, 1.04

A)

B)

C)

D)

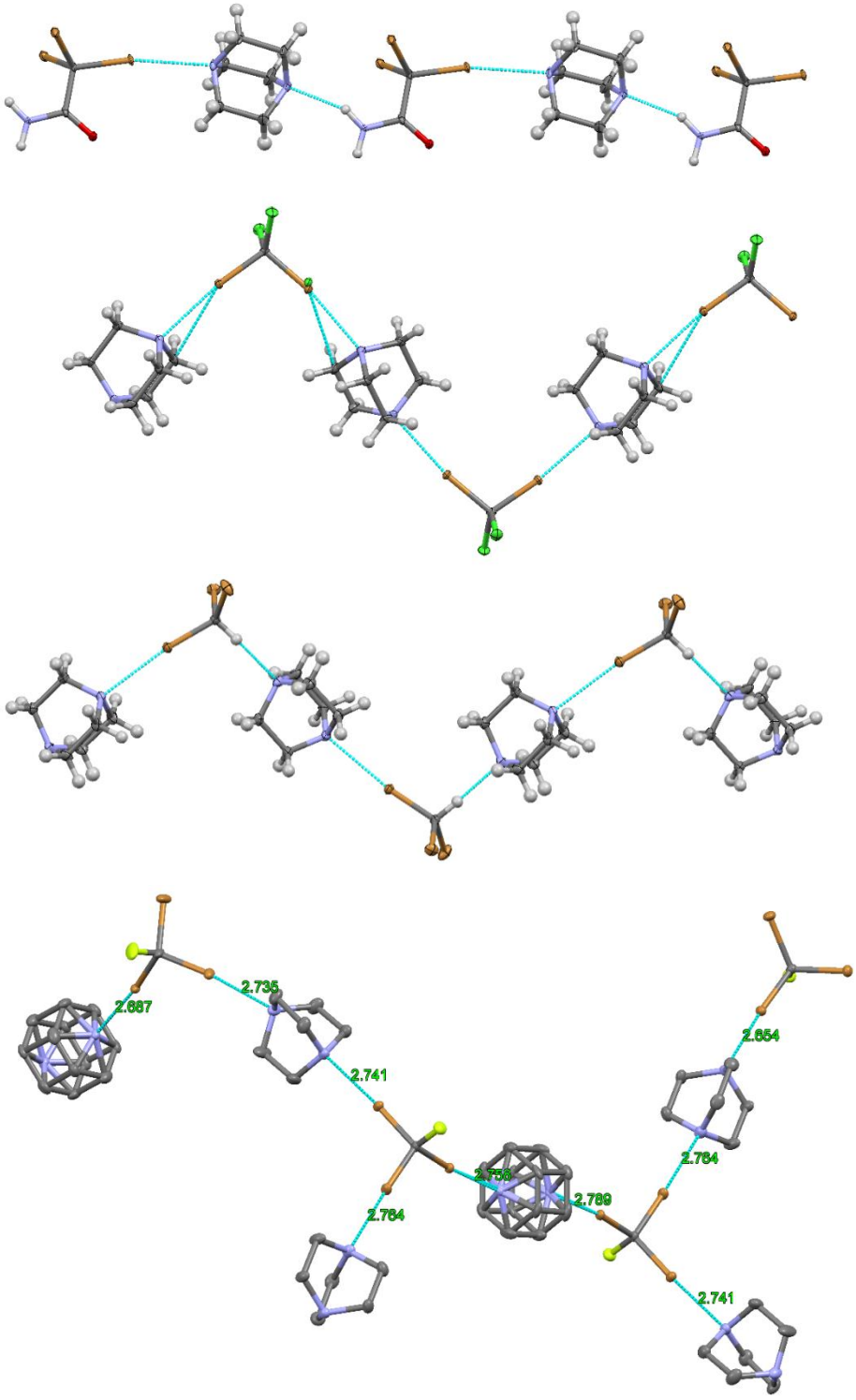
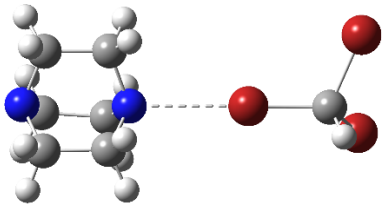


Figure S8. Fragments of the X-ray structures of CBr_3CONH_2· DABCO (A), $CBrCl_3$· DABCO (B), $CHBr_3$·DABCO (C) and CBr_3F·DABCO (D)

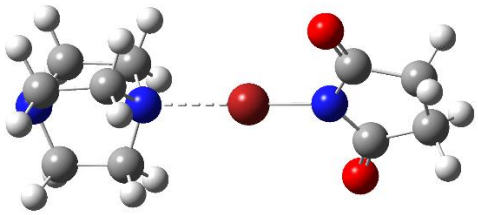
B) Quantum-mechanical computations

Quantum-mechanical calculations were carried out using the Gaussian 09 suite of programs. The geometries of all bromo-substituted molecules R-Br and [R-Br, DABCO] complexes were optimized in the gas phase via DFT calculations with a M06-2X functional and a 6-311+G(d,p) basis set. Geometry optimizations were carried out without constraints using the default convergence criteria for Gaussian 09 except in cases that required tighter convergence criteria to obtain true minima (as indicated by the absence of imaginary frequencies). The energies of interaction were determined by subtracting the sum of the energies of isolated R-Br and DABCO species from the energy of their complexes and adding basis set superposition error (BSSE): $\Delta E = E_{complex} - [E_{R\text{-}Br} + E_{DABCO}] + BSSE$, in which $E_{complex}$, $E_{R\text{-}Br}$, and E_{DABCO} are sums of the electronic and zero-point energies of the optimized complex, R-Br electrophile and DABCO, respectively. The BSSE values for the complexes were determined by the counterpoise method. Zero-point energies (ZPE) and thermal corrections were taken from unscaled vibrational frequencies. Atomic charges were calculated by means of the natural population analysis phase of the NBO analysis implemented in the Gaussian 09 suite of programs. Absorption bands maxima and extinction coefficients were obtained by TD DFT calculations in acetonitrile. Energies, geometric and spectral characteristics and atomic coordinates of halogen-bonded associates are listed below.

A



B



C

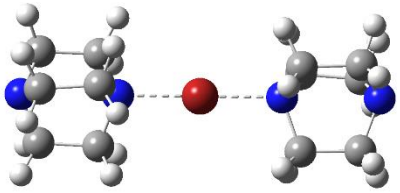


Figure S9. Typical structures of the halogen bonded complexes resulted from the M062X/6-311+G(dp) optimizations

Table S2. Energies (in Hartrees) of the halogen-bonded [R-Br, DABCO] complexes and R-Br electrophiles from the M06-2X/6-311+G(dp) computations (gas phase).

R-Br	[R-Br, DABCO]			R-Br	
	E	ZPE	BSSE	E	ZPE
$CH_2Br(NH_2)$	-3014.69138	0.24185	0.000480	-2669.42	0.056178
CH_3Br	-2959.33889	0.22321	0.000479	-2614.07	0.037552
CH_2BrF	-3058.57411	0.21658	0.000607	-2713.3	0.030878
CH_2Br_2	-5532.90646	0.21436	0.000670	-5187.63	0.028588
BrCCH	-2996.15731	0.20488	0.000674	-2650.88	0.019023
$C_6Br_2F_4$	-6121.55107	0.23442	0.001031	-5776.27	0.048683
$C_2Br_2F_4$	-5969.17889	0.21071	0.001059	-5623.9	0.024943
$CHBr_3$	-8106.46850	0.20424	0.000872	-7761.19	0.018454
CBr_3CONH_2	-8275.15563	0.23029	0.001039	-7929.88	0.044194
CBr_3F	-8205.70238	0.19562	0.000919	-7860.42	0.009678
CBr_3COCBr_3	-15979.76143	0.21025	0.001375	-15634.5	0.024439
$CBrCl_3$	-4338.10963	0.19519	0.001454	-3992.83	0.009204
CBr_4	-10680.02329	0.19332	0.001131	-10334.7	0.007299
CBr_3CN	-8198.68717	0.20226	0.001079	-7853.4	0.016089
CBr_3NO_2	-8310.93445	0.20616	0.001302	-7965.65	0.020003
$CBr(NO_2)_3$	-3572.74659	0.23213	0.001877	-3227.46	0.045541
NBrSIM	-3279.44700	0.26874	0.001548	-2934.16	0.082078
NBrPIM	-3431.84860	0.29277	0.001517	-3086.56	0.106143
Br_2	-5493.61488	0.18782	0.001592	-5148.32	0.000775
NBrSAC	-3867.05699	0.29330	0.002018	-3521.76	0.106133
BrCl	-3379.63067	0.18828	0.001877	-3034.34	0.001026
BrF	-3019.24363	0.18947	0.002272	-2673.93	0.001596
DABCO-Br^+	-3264.49822	0.37598	0.001961	-2919.17	0.188569
pyrazine-Br^+	-3183.48006	0.26735	0.002272	-2838.14	0.079482
F_5Pyr-Br^+	-3663.61456	0.23899	0.002564	-3318.24	0.051318

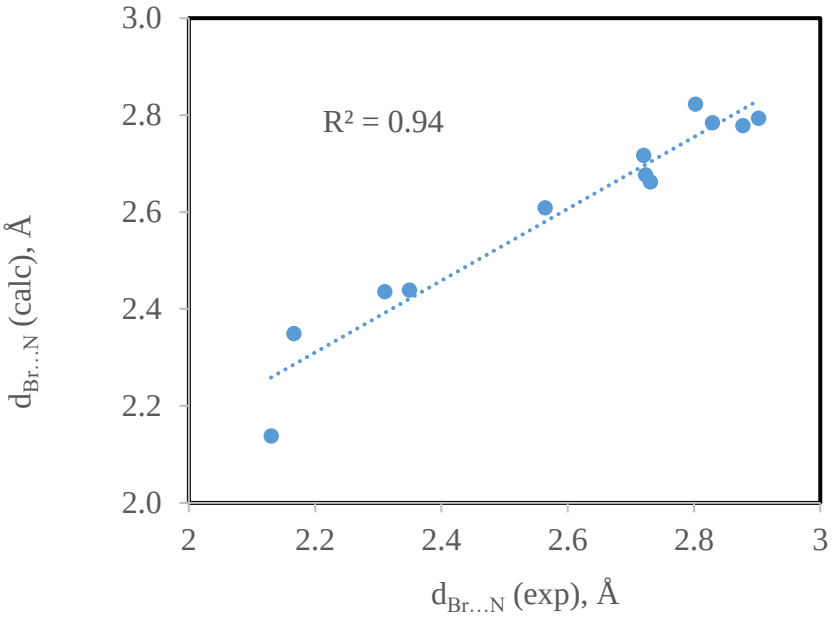
Table S3. Bond distances (in Å) and angles (in deg) in the halogen-bonded [R-Br, DABCO] complexes and R-Br electrophiles from the M06-2X/6-311+G(dp) computations (gas phase).

	[R-Br, DABCO]				R-Br
R-Br	d(N···Br)	d(X-Br)	∠X-Br..N	∠N-N-Br	d(X-Br)
$CH_2Br(NH_2)$	3.154	2.019	172.0	154.3	2.037
CH_3Br	3.004	1.946	173.7	163.1	1.942
CH_2BrF	2.949	1.939	175.7	170.0	1.940
CH_2Br_2	2.891	1.934	176.7	170	1.931
BrCCH	2.823	1.809	179.7	179.3	1.793
$C_6Br_2F_4$	2.794	1.886	179.6	179.1	1.897
$C_2Br_2F_4$	2.785	1.939	178.4	179.3	1.933
$CHBr_3$	2.778	1.938	179.1	179.0	1.931
CBr_3CONH_2	2.727	1.964	178.1	177.1	1.953
CBr_3F	2.717	1.946	178.0	179.2	1.938
CBr_3COCBr_3	2.692	1.951	173.6	170.5	1.936
$CBrCl_3$	2.677	1.963	179.7	179.4	1.949
CBr_4	2.662	1.959	178.8	178.1	1.942
CBr_3CN	2.617	1.971	179.3	179.4	1.944
CBr_3NO_2	2.609	1.964	179.7	179.7	1.927
$CBr(NO_2)_3$	2.511	1.937	179.9	179.5	1.873
NBrSIM	2.439	1.902	179.9	179.8	1.836
NBrPIM	2.436	1.898	179.9	179.8	1.831
Br_2	2.350	2.411	180.0	180.0	2.294
NBrSAC	2.320	1.944	179.6	179.4	1.834
BrCl	2.309	2.281	180.0	180.0	2.158
BrF	2.213	1.880	180.0	180.0	1.782
DABCO-Br^+	2.138	2.138	180.0	180.0	1.918
pyrazine-Br^+	2.046	2.234	180.0	180.0	1.870
F_5Pyr-Br^+	1.946	2.600	179.9	180.0	1.871

Table S4. Wavelength and extinction coefficients of the absorption bands maxima of the halogen-bonded [R-Br, DABCO] complexes (from TD DFT computations in acetonitrile)

R-Br	λ_{max}, nm	log(ε)
$CH_2Br(NH_2)$	227	3.51
CH_3Br	224	3.48
CH_2BrF	223	3.54
CH_2Br_2	238	3.79
BrCCH	218	3.29
$C_6Br_2F_4$[e]	249	3.49
$C_2Br_2F_4$	249	3.96
$CHBr_3$	273	3.86
CBr_3CONH_2	269	4.02
CBr_3F	290	3.94
CBr_3COCBr_3	305	3.28
$CBrCl_3$	266	4.09
CBr_4	313	3.92
CBr_3CN	269	4.02
CBr_3NO_2	288	3.99
$CBr(NO_2)_3$	335	3.96
NBrSIM	235	4.04
NBrPIM	252	3.43
Br_2	303	4.33
NBrSAC	244	4.31
BrCl	281	4.26
BrF	232	3.87
DABCO-Br^+	257	4.34
pyrazine-Br^+	252	4.00
F_5Pyr-Br^+	275	3.48

A



B

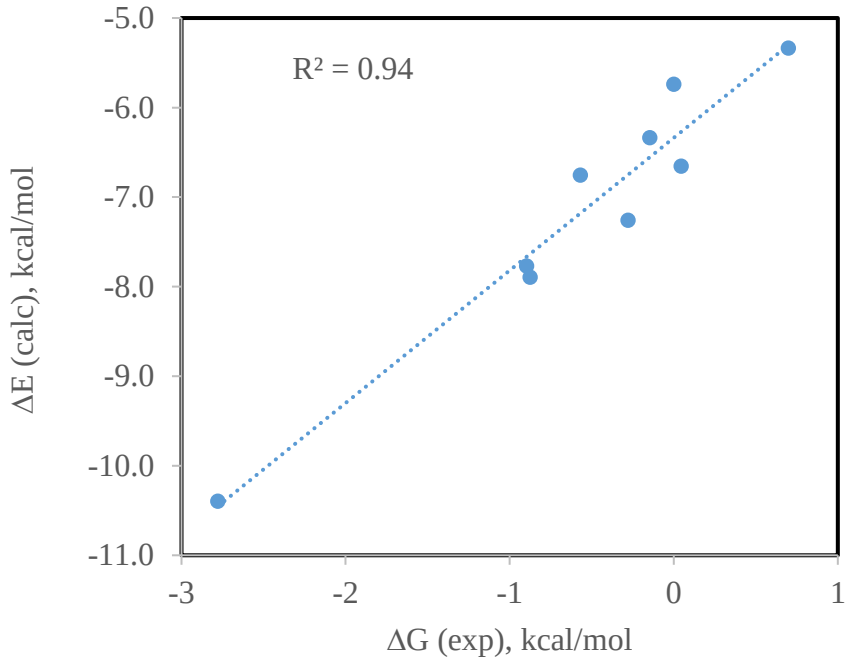


Figure S10. Correlations between (A) the calculated and experimental (from X-ray crystallographic measurements) N···Br distances and (B) between the calculated interaction energies and experimental free energies of complex formation (calculated as ΔG = -RTlogK, where K is the formation constant measured in acetonitrile).

Atomic coordinates of the halogen-bonded [R-Br, DABCO] complexes from the M06-2X/6-311+G(dp) computations (gas phase)

R-Br	Coordinates			
$CH_2Br(NH_2)$	Br	1.99844800	-0.02239600	-0.01312100
	C	3.94065500	-0.57438200	0.01803900
	N	-1.12565500	0.40932100	-0.01740100
	C	-1.37375200	-0.51979900	-1.12530800
	C	-1.41286300	-0.27653200	1.24699500
	C	-2.02546900	1.55914500	-0.15018000
	N	-3.56648500	-0.37530000	0.02235300
	H	-1.05447800	-0.04114900	-2.05487900
	H	-0.73755000	-1.39555800	-0.97191200
	H	-0.66925600	-1.06581000	1.38478400
	H	-1.28038100	0.44625700	2.05670100
	H	-1.76499500	2.29297700	0.61678100
	H	-1.84004900	2.01838600	-1.12480800
	C	-2.88271900	-0.90569500	-1.16323600
	H	-3.01872400	-1.98994500	-1.18413200
	H	-3.37763800	-0.49325200	-2.04656900
	C	-2.86312400	-0.84590400	1.22153900
	H	-3.43240200	-0.53378500	2.10079200
	H	-2.86104700	-1.93894000	1.19992500
	C	-3.50590100	1.09011500	-0.01482900
	H	-4.11547100	1.44043500	-0.85168800
	H	-3.95989600	1.46688600	0.90560000
	H	4.04903500	-1.19284000	-0.86688900
	H	4.02590200	-1.17229800	0.91946300
	N	4.86776100	0.48655300	0.01776500
	H	4.78882100	1.07881600	0.83455200
	H	4.81213900	1.05800100	-0.81560500
CH_3Br	Br	2.30900200	0.09432000	0.00031600
	C	4.22633500	-0.23759900	-0.00070200
	N	-0.68934400	0.27990400	-0.00223900
	C	-1.49416400	1.50476900	0.04044900
	C	-1.02774600	-0.47245100	-1.21525900
	C	-1.00723800	-0.54202700	1.17055000
	N	-3.18156900	-0.31202100	0.00216600
	H	-1.26729700	2.02181800	0.97648200
	H	-1.17961700	2.15332500	-0.78104200
	H	-0.83233700	0.17454400	-2.07470200
	H	-0.35125500	-1.32826400	-1.28675300
	H	-0.43593900	-1.47081900	1.08974800
	H	-0.65692700	-0.01746600	2.06337100
	C	-3.00741600	1.14344300	-0.05965000
	H	-3.43793900	1.49224800	-1.00198800
	H	-3.58144000	1.59484000	0.75345200
	C	-2.52035500	-0.91668500	-1.16006100
	H	-2.60933300	-2.00232800	-1.06816000
	H	-3.06159800	-0.61564600	-2.06050800
	C	-2.54072200	-0.81315500	1.22358800
	H	-3.00490000	-0.30976200	2.07574600
	H	-2.75586600	-1.88088200	1.31305800
	H	4.65820700	0.27099300	-0.85713000
	H	4.63886000	0.15235800	0.92471300

	H	4.38653700	-1.30912300	-0.07034200
CH_2BrF	Br	-1.95371000	-0.30022900	-0.01827100
	C	-3.89009000	-0.23524800	0.05694900
	N	0.99272200	-0.19045700	-0.06162400
	C	1.52971600	-0.64913100	1.22421600
	C	1.69788300	-0.87858700	-1.14811600
	C	1.21881800	1.25459300	-0.18473100
	N	3.49870100	0.31537100	0.06762600
	H	0.93040300	-0.20615600	2.02409300
	H	1.39820600	-1.73338000	1.27387200
	H	1.44311300	-1.94070100	-1.10663000
	H	1.31934000	-0.48371100	-2.09464000
	H	0.72554300	1.60287100	-1.09601000
	H	0.72682900	1.74168400	0.66159000
	C	3.03187800	-0.24937700	1.33859100
	H	3.65746800	-1.11093900	1.58457200
	H	3.18470300	0.50356600	2.11604200
	C	3.23317500	-0.64934900	-1.00514100
	H	3.66824300	-0.26524200	-1.93103400
	H	3.75217000	-1.57858600	-0.75606400
	C	2.74903300	1.54656200	-0.20668400
	H	3.02478200	2.29308300	0.54211200
	H	3.06830500	1.92275700	-1.18200700
	H	-4.20308900	-0.66516300	1.00458400
	H	-4.27669600	-0.78441600	-0.79730600
	F	-4.32243300	1.05568600	-0.01069000
CH_2Br_2	Br	-0.94885400	0.76137800	-0.00132300
	C	-2.86848400	0.99694400	0.00410100
	N	1.89522700	0.24527800	-0.00526600
	C	2.10202600	-0.65054300	-1.14948600
	C	2.84040400	1.36352000	-0.09478900
	C	2.14741300	-0.49821300	1.23479300
	N	4.29531300	-0.64184900	0.00577000
	H	1.32831500	-1.42243900	-1.12429300
	H	1.95523900	-0.06590700	-2.06163700
	H	2.58090400	1.96477500	-0.96986100
	H	2.70273800	1.98959700	0.79073300
	H	1.89445000	0.14739600	2.07988200
	H	1.46420000	-1.35158400	1.25575700
	C	3.53357800	-1.26242900	-1.08383100
	H	4.07802200	-1.10683700	-2.01837200
	H	3.49740900	-2.33869900	-0.89717300
	C	4.29593200	0.81247000	-0.18521100
	H	4.94066400	1.26054600	0.57479800
	H	4.74006500	1.02225500	-1.16164200
	C	3.63735300	-0.95220000	1.27977900
	H	3.72250000	-2.02654000	1.45987700
	H	4.18553900	-0.43901700	2.07402000
	Br	-3.85845300	-0.66954200	-0.00014700
	H	-3.15073600	1.53899500	-0.89016600
	H	-3.14666400	1.53188600	0.90390000
BrCCH	Br	-2.01108700	0.00673900	-0.00249200
	N	0.81184500	0.01065100	-0.00424500
	C	1.32441400	1.03209000	-0.92660400
	C	1.30885100	0.29382400	1.34845800
	C	1.30027600	-1.30780200	-0.42842500

	N	3.36942600	-0.01402800	0.00525000
	H	0.87304900	0.86537200	-1.90821600
	H	0.98480600	2.00717500	-0.56726000
	H	0.86388800	1.23286600	1.68787300
	H	0.95017100	-0.50005700	2.00906200
	H	0.83799000	-2.06591900	0.20930200
	H	0.95368300	-1.47935800	-1.45103800
	C	2.88001000	0.95142600	-0.98430100
	H	3.33754700	1.92161000	-0.77680100
	H	3.22439500	0.62654200	-1.96928700
	C	2.86568300	0.36594200	1.32916800
	H	3.30525600	-0.30405300	2.07189000
	H	3.21871400	1.37740600	1.54536100
	C	2.85525200	-1.34456900	-0.33473500
	H	3.30432100	-1.65744300	-1.28028600
	H	3.18999200	-2.04152500	0.43763600
	C	-3.82032800	-0.00559100	0.00188000
	C	-5.02086500	-0.01414700	0.00519700
	H	-6.08441200	-0.02188700	0.00811700
$C_6Br_2F_4$[e]	Br	-1.05190700	-0.00824100	-0.01849500
	N	-3.84557400	-0.00636400	-0.01178900
	C	-4.32258000	0.03340900	1.37677700
	C	-4.34737900	1.17524500	-0.72552800
	C	-4.36353400	-1.21692900	-0.66268500
	N	-6.40200900	0.01210900	0.02852300
	H	-3.86281300	-0.79544200	1.92135300
	H	-3.96480000	0.96393700	1.82552900
	H	-3.87670300	2.06239600	-0.29390000
	H	-4.02038600	1.10012500	-1.76603500
	H	-3.92262400	-1.28555400	-1.66054200
	H	-4.01645100	-2.07930300	-0.08740600
	C	-5.87826500	-0.05363000	1.39673000
	H	-6.31571600	0.76381300	1.97464800
	H	-6.21736500	-0.99239000	1.84167600
	C	-5.90056600	1.23153000	-0.61377600
	H	-6.36808300	1.32216000	-1.59701900
	H	-6.22435200	2.08516700	-0.01320100
	C	-5.91939300	-1.15239700	-0.72105900
	H	-6.37182700	-2.05060200	-0.29433100
	H	-6.27425100	-1.05994200	-1.75051800
	C	0.83370200	-0.00421800	-0.01017100
	C	1.55031700	-1.19311300	-0.00683200
	C	1.54529000	1.18767500	-0.00689100
	C	2.93634400	-1.19338600	-0.00045900
	C	2.93131600	1.19378500	-0.00060200
	C	3.64289000	0.00170500	0.00257600
	F	0.91809300	-2.36105200	-0.00941800
	F	0.90816300	2.35297600	-0.00955100
	F	3.56786800	2.35790300	0.00226500
	F	3.57782000	-2.35479700	0.00256800
	Br	5.51396700	0.00572900	0.01110500
$C_2Br_2F_4$	Br	0.12921900	-0.42290300	-0.00047500
	C	-1.78276400	-0.74430800	-0.00013100
	N	2.88706900	-0.03774200	-0.00062300
	C	3.17227900	1.39603400	-0.14282400
	C	3.46388100	-0.51943400	1.26132300

	C	3.50276800	-0.76369900	-1.11919800
	N	5.41390600	0.34842100	0.00106500
	H	2.65691100	1.76146000	-1.03483600
	H	2.74229800	1.90878600	0.72167200
	H	2.93074700	-0.04075900	2.08675600
	H	3.27671800	-1.59459700	1.32519700
	H	3.20308700	-1.81286200	-1.05391600
	H	3.09061200	-0.35848300	-2.04707800
	C	4.71249800	1.61459200	-0.23409100
	H	5.05586800	2.34284100	0.50430200
	H	5.00316800	1.98170100	-1.22144400
	C	4.98835200	-0.19772000	1.29376500
	H	5.57992500	-1.09199200	1.50302500
	H	5.22132200	0.54129000	2.06429300
	C	5.05128400	-0.59937700	-1.05752600
	H	5.45049100	-0.22970400	-2.00486800
	H	5.54259700	-1.55085700	-0.83975000
	C	-2.57163000	0.58379700	-0.00092500
	Br	-4.48147300	0.25638800	0.00098300
	F	-2.25002600	1.29022000	-1.08332500
	F	-2.24829100	1.29243500	1.07950400
	F	-2.12602400	-1.44896400	-1.08303700
	F	-2.12584900	-1.44734500	1.08390500
$CHBr_3$	Br	-2.99548700	-1.60096800	-0.16392000
	Br	-0.25483300	0.00081500	0.33757600
	C	-2.17978800	0.00003100	0.56055100
	N	2.50998700	-0.00031300	0.06335300
	C	3.16444700	0.13797800	1.36997800
	C	2.93792500	-1.25947100	-0.55869200
	C	2.90933000	1.12096700	-0.79629000
	N	5.04805800	0.00031200	-0.23520100
	H	2.76058800	1.02561700	1.86381200
	H	2.89027700	-0.73123000	1.97373700
	H	2.54604300	-2.08749200	0.03766700
	H	2.47558800	-1.31634300	-1.54765300
	H	2.33781500	1.06067700	-1.72606100
	H	2.62234200	2.04698200	-0.29102800
	C	4.70707000	0.23700400	1.17138200
	H	5.23585300	-0.49686000	1.78414800
	H	5.07940200	1.22727800	1.44529700
	C	4.49340000	-1.29364600	-0.64686000
	H	4.83048800	-1.50701300	-1.66391000
	H	4.91109000	-2.06197300	0.00851500
	C	4.44495000	1.05732200	-1.05404300
	H	4.93006000	2.00489100	-0.80830800
	H	4.66247900	0.83580400	-2.10183100
	Br	-2.99705000	1.60011200	-0.16418100
	H	-2.39442600	0.00000400	1.62077600
CBr_3CONH_2	Br	-2.68009200	-1.43890600	-0.91886900
	Br	0.02941200	-0.05159400	0.09504400
	C	-1.93196000	0.00966600	0.16975800
	N	2.75549700	-0.04862100	0.00722600
	C	3.20986300	1.27218800	0.46198600
	C	3.34131500	-1.08288700	0.86865900
	C	3.20196000	-0.26175900	-1.37553000
	N	5.30450600	0.07457400	-0.10623900

	H	2.68542300	2.03391500	-0.12047200
	H	2.90640400	1.38758600	1.50576900
	H	2.92056200	-0.97281400	1.87147700
	H	3.02827100	-2.05612500	0.48129100
	H	2.77017400	-1.19920000	-1.73540200
	H	2.79210700	0.54740100	-1.98558400
	C	4.75558500	1.37419000	0.29521100
	H	5.23708000	1.68092700	1.22658200
	H	5.02413900	2.10403600	-0.47240300
	C	4.89312500	-0.93712500	0.87212000
	H	5.38217900	-1.88125600	0.62113100
	H	5.25919900	-0.62460100	1.85317500
	C	4.75955300	-0.28555200	-1.41939100
	H	5.14749500	0.41729700	-2.16022500
	H	5.13368100	-1.27931300	-1.67759000
	Br	-2.57401800	1.70035300	-0.49918900
	C	-2.33756900	-0.15519300	1.66564900
	O	-2.67276400	0.79261500	2.32500600
	N	-2.20802700	-1.41129000	2.15093500
	H	-2.39544600	-1.55118300	3.13041700
	H	-1.95978400	-2.19625400	1.57302400
CBr_3F	Br	-2.85521100	-1.60379500	-0.30983600
	Br	-0.13061600	0.01251600	0.23078400
	C	-2.06392600	0.00016200	0.45469100
	N	2.57799400	0.01314200	0.01168800
	C	3.06061700	1.33849800	-0.39787100
	C	3.16483600	-0.33296000	1.31315100
	C	2.99542900	-0.98152400	-0.98523100
	N	5.12583200	-0.01301100	-0.16858500
	H	2.53759000	1.62635900	-1.31343400
	H	2.77987200	2.05083800	0.38229600
	H	2.76331900	0.35280100	2.06357700
	H	2.82947900	-1.34066800	1.57204600
	H	2.54250700	-1.94107900	-0.72291000
	H	2.58737100	-0.67559400	-1.95212400
	C	4.60449100	1.28674600	-0.60354900
	H	5.10827600	2.07087400	-0.03374000
	H	4.86848100	1.41993800	-1.65552800
	C	4.71792300	-0.24755500	1.22040200
	H	5.18878900	-1.16947300	1.56920700
	H	5.10635600	0.57340900	1.82804300
	C	4.55129300	-1.06297700	-1.01585600
	H	4.93622300	-0.93918500	-2.03067500
	H	4.90477200	-2.02723200	-0.64256500
	Br	-2.87681300	1.59115700	-0.31410800
	F	-2.34126200	0.00000500	1.76447700
CBr_3COCBr_3	Br	1.64978300	1.92861900	1.71396700
	Br	-0.89809300	1.07103800	-0.08121900
	C	1.01291800	1.46545600	-0.07922900
	N	-3.45789900	0.23864900	-0.04020600
	C	-4.44882800	0.97834900	-0.83208100
	C	-3.35148200	-1.13343500	-0.55664700
	C	-3.89318000	0.19213300	1.36203000
	N	-5.72680300	-0.92218200	0.12025900
	H	-4.45563400	2.01595500	-0.48960200
	H	-4.11584400	0.97365400	-1.87301500

	H	-2.94560700	-1.08396100	-1.57069500
	H	-2.62368800	-1.66716400	0.06164500
	H	-3.10397000	-0.28900100	1.94628600
	H	-3.98814300	1.22159300	1.71691800
	C	-5.84649200	0.30625600	-0.67081900
	H	-6.27892700	0.05108300	-1.64101200
	H	-6.54808800	0.96976300	-0.15953800
	C	-4.75397100	-1.81085400	-0.52330300
	H	-4.72762000	-2.75217600	0.03032200
	H	-5.11273800	-2.02954900	-1.53193900
	C	-5.24328200	-0.57993300	1.46138300
	H	-6.00776100	0.01921000	1.96135000
	H	-5.12838000	-1.50848900	2.02569100
	Br	1.33818700	2.96682700	-1.26723600
	C	1.92489500	0.28503500	-0.52203500
$CBrCl_3$	Br	-0.66452000	-0.00346900	-0.00963800
	C	-2.62719900	0.00044700	0.00153200
	N	2.01220600	-0.00316700	-0.01052700
	C	2.50510100	1.37790500	-0.09688100
	C	2.49857200	-0.61326800	1.23405500
	C	2.52053500	-0.77017900	-1.15550800
	N	4.56512900	0.00383400	0.01272400
	H	2.04850400	1.85088500	-0.96998900
	H	2.15527300	1.91196900	0.79039600
	H	2.02585500	-0.09997200	2.07526600
	H	2.16171700	-1.65306500	1.24827600
	H	2.05977100	-1.76105500	-1.13634500
	H	2.18757500	-0.26708000	-2.06701800
	C	4.06052900	1.36601100	-0.18857900
	H	4.50827700	2.01707300	0.56567600
	H	4.40201300	1.70989600	-1.16794700
	C	4.05226900	-0.50877200	1.28735400
	H	4.50978200	-1.48188700	1.47967000
	H	4.37628900	0.17195200	2.07833400
	C	4.07468300	-0.84959400	-1.07425500
	H	4.53871100	-0.52358600	-2.00789600
	H	4.40913200	-1.87095800	-0.87686100
	Cl	-3.23863100	-1.20324500	-1.15420600
	Cl	-3.22795600	1.60861900	-0.45872600
	Cl	-3.22005900	-0.39965000	1.62846500
CBr_4	Br	-2.44575400	1.81372800	-0.16022700
	Br	0.20544300	0.03652600	0.02226700
	C	-1.75320500	0.00078800	0.00069200
	N	2.86753400	0.03760300	0.02139300
	C	3.35259300	-0.87993200	1.06076000
	C	3.32759100	-0.43103300	-1.29254100
	C	3.40582300	1.38067000	0.27283000
	N	5.41828400	-0.03731000	-0.02067800
	H	2.91981700	-0.57349200	2.01651800
	H	2.97109900	-1.87780000	0.82897000
	H	2.83674500	-1.38373300	-1.50715600
	H	2.98962100	0.29110600	-2.04036100
	H	2.95469800	2.07107500	-0.44432500
	H	3.08616400	1.68553800	1.27257800
	C	4.91041600	-0.84760900	1.09111300
	H	5.33057100	-1.85243800	1.00726600

	H	5.27918500	-0.41075600	2.02229700
	C	4.87987200	-0.56579700	-1.27808300
	H	5.33401200	-0.01831200	-2.10708500
	H	5.18720800	-1.61091800	-1.36294900
	C	4.95902300	1.34489600	0.14882100
	H	5.43815600	1.76311100	1.03692000
	H	5.30035600	1.92110500	-0.71453600
	Br	-2.41814000	-0.79369600	1.64990500
	Br	-2.37357900	-1.05708500	-1.51293600
CBr_3CN	Br	-2.74652700	-1.60317500	-0.49334000
	Br	-0.03600600	0.00720400	0.17464700
	C	-2.00177100	0.00002700	0.32455500
	N	2.57574400	0.00739400	0.00818100
	C	3.05738400	1.33587500	-0.39573300
	C	3.14085800	-0.33411300	1.32172000
	C	3.01243100	-0.98799500	-0.98103500
	N	5.12341600	-0.00733800	-0.12967900
	H	2.54495700	1.62041100	-1.31815000
	H	2.76295600	2.04624800	0.38093800
	H	2.72050400	0.34936500	2.06354700
	H	2.80762500	-1.34386700	1.57446500
	H	2.55637600	-1.94779200	-0.72575800
	H	2.62125600	-0.68252800	-1.95488000
	C	4.60392300	1.28747100	-0.57986300
	H	5.09604600	2.07752900	-0.00844900
	H	4.88092700	1.41517400	-1.62902800
	C	4.69440900	-0.23683600	1.25347500
	H	5.16538000	-1.15303400	1.61625300
	H	5.06553300	0.59054900	1.86288000
	C	4.56873700	-1.06418000	-0.98083000
	H	4.97146700	-0.94608300	-1.98921900
	H	4.91713200	-2.02509800	-0.59486900
	Br	-2.75888900	1.59583500	-0.49649200
	C	-2.36063800	0.00007400	1.73052400
	N	-2.62092700	0.00022700	2.84962300
CBr_3NO_2	Br	-2.63182500	-1.58446400	-0.65751200
	Br	0.07294400	-0.00532800	0.06427900
	C	-1.88963100	0.00015000	0.13583400
	N	2.68062600	-0.00635500	-0.01923400
	C	3.15352100	1.25014100	-0.61777700
	C	3.21614000	-0.12572400	1.34467300
	C	3.15577300	-1.13790100	-0.82797700
	N	5.23045100	0.00270800	-0.09431900
	H	2.66265400	1.37406300	-1.58632100
	H	2.82679100	2.06923100	0.02785300
	H	2.76952900	0.66075600	1.95798400
	H	2.88856300	-1.08747800	1.74741700
	H	2.70859500	-2.05324600	-0.43244600
	H	2.78313700	-0.99845400	-1.84602500
	C	4.70511700	1.20230300	-0.75309600
	H	5.16956300	2.08016900	-0.29865600
	H	5.00942300	1.17152000	-1.80198800
	C	4.76974300	-0.01613700	1.29739300
	H	5.24195200	-0.85790300	1.80852500
	H	5.11573800	0.90115700	1.77950100
	C	4.71269300	-1.18338200	-0.78283500

	H	5.13747500	-1.21470900	-1.78859700
	H	5.06648300	-2.06640400	-0.24553800
	Br	-2.62448900	1.58392700	-0.66887900
	N	-2.22170600	0.01103700	1.66883700
	O	-2.33708800	-1.05916000	2.20093900
	O	-2.25387100	1.08892600	2.19755300
$CBr(NO_2)_3$	Br	0.22990100	-0.00379500	0.00481600
	C	2.16650500	-0.00002300	-0.00035100
	N	-2.28152900	-0.00513300	0.00735500
	C	-2.76900100	-0.09085200	-1.37941400
	C	-2.78647100	-1.15779000	0.77179500
	C	-2.77546000	1.23908600	0.62048800
	N	-4.82985200	0.00582500	-0.00836900
	H	-2.28734300	0.69764700	-1.96270500
	H	-2.44415100	-1.05195700	-1.78567100
	H	-2.31362500	-2.06258000	0.38236300
	H	-2.46555600	-1.03357100	1.80902100
	H	-2.30670600	1.34884600	1.60134300
	H	-2.44110400	2.07133600	-0.00394100
	C	-4.32056100	0.04499400	-1.38193200
	H	-4.78600300	-0.76198500	-1.95147800
	H	-4.63220800	0.99079900	-1.83077800
	C	-4.33825500	-1.20913700	0.64699400
	H	-4.80992100	-1.29345800	1.62814100
	H	-4.65687800	-2.06702400	0.05058600
	C	-4.32856200	1.17508400	0.71875300
	H	-4.78715100	2.07235100	0.29831800
	H	-4.65400800	1.09166100	1.75812700
	N	2.74246900	0.95981600	-1.04941000
	O	3.64667100	1.66523500	-0.69303400
	O	2.23729800	0.89239300	-2.13484600
NBrSIM	Br	-0.55007200	0.00389500	-0.00039300
	N	-2.45208700	0.00028800	-0.00058700
	C	-3.20858100	1.16645000	0.00001600
	O	-2.77067200	2.28351200	0.00005400
	C	-4.67725300	0.76025100	0.00080700
	H	-5.15080200	1.19761200	-0.87851600
	H	-5.14953200	1.19688400	0.88118000
	C	-4.67385000	-0.76962400	0.00027600
	H	-5.14473200	-1.20908500	0.87998100
	H	-5.14484700	-1.20837300	-0.87973600
	C	-3.20337500	-1.16921800	-0.00002700
	O	-2.76050600	-2.28435200	0.00022900
	N	1.88889200	0.00334300	0.00031600
	C	2.37874900	-1.14170100	-0.78468700
	H	2.04214200	-1.00246600	-1.81471900
	H	1.90362800	-2.04659100	-0.39933300
	C	3.93123700	-1.20027900	-0.68083200
	H	4.25493300	-2.07462500	-0.11154500
	H	4.39094100	-1.25950900	-1.66961900
	N	4.43715800	-0.00453900	-0.00014900
	C	3.93570200	0.00570800	1.37709300
	H	4.26508600	0.93425400	1.84900600
	H	4.39288600	-0.82346800	1.92112500
	C	2.38248900	-0.10638400	1.38270900
	H	2.04204800	-1.06618600	1.77841200

	H	1.91423300	0.68344200	1.97439600
	C	2.38594500	1.25361400	-0.59731300
	H	2.04986500	2.07798900	0.03590800
	H	1.91501200	1.37349200	-1.57551500
	C	3.93850700	1.18548500	-0.69605300
	H	4.26479700	1.12843900	-1.73706800
	H	4.40110900	2.06913900	-0.25144800
NBrPIM	Br	0.38971400	0.00456700	-0.00107000
	N	2.82543500	0.00288400	0.00114800
	C	3.31949200	-0.10265300	1.38385500
	C	3.31485300	-1.14484500	-0.78036200
	C	3.32305400	1.25107400	-0.60061800
	N	5.37377800	-0.00601100	0.00005700
	H	2.85111200	0.68867700	1.97339500
	H	2.97941000	-1.06138400	1.78240500
	H	2.83920300	-2.04831700	-0.39231100
	H	2.97845200	-1.00848100	-1.81084000
	H	2.85144100	1.36840900	-1.57879800
	H	2.98826500	2.07752500	0.03059900
	C	4.87261400	0.00979400	1.37735800
	H	5.33007100	-0.81697000	1.92480500
	H	5.20186400	0.94036900	1.84534100
	C	4.86719800	-1.20414400	-0.67590600
	H	5.32702100	-1.26777700	-1.66435000
	H	5.19010000	-2.07639900	-0.10297900
	C	4.87543400	1.18147300	-0.70034300
	H	5.33895200	2.06668400	-0.25982600
	H	5.20071300	1.11989300	-1.74140900
	N	-1.50868900	0.00234600	-0.00223900
	C	-2.27939200	-1.16420000	-0.00101600
	O	-1.86727600	-2.29081000	-0.00049600
	C	-2.28299100	1.16654000	-0.00105900
	O	-1.87435200	2.29437900	-0.00072000
	C	-3.70350400	-0.69456500	-0.00035100
	C	-3.70565000	0.69244200	-0.00016300
	C	-4.87744100	-1.42292800	0.00067400
	C	-4.88187200	1.41710600	0.00100200
	C	-6.07385200	-0.70265800	0.00180100
	H	-4.86033600	-2.50599900	0.00062400
	C	-6.07601900	0.69308500	0.00196800
	H	-4.86825100	2.50022300	0.00118400
	H	-7.01819900	-1.23369400	0.00261000
	H	-7.02201500	1.22117800	0.00291200
Br_2	Br	-1.05839200	-0.00000500	-0.00007500
	N	1.29112400	0.00007700	-0.00007500
	C	1.77928100	0.15254400	1.38144000
	C	1.77933800	-1.27268700	-0.55868300
	C	1.77942800	1.12023300	-0.82288600
	N	3.83328300	-0.00003500	0.00011800
	H	1.30414200	1.03594400	1.81219300
	H	1.44152900	-0.71875500	1.94640000
	H	1.30406400	-2.08741800	-0.00912300
	H	1.44177500	-1.32630200	-1.59579900
	H	1.30434300	1.05186700	-1.80335300
	H	1.44183300	2.04518100	-0.35073300
	C	3.33232900	0.26968000	1.35011900

	H	3.79188900	-0.43826900	2.04252000
	H	3.65524200	1.27274900	1.63699400
	C	3.33247000	-1.30407300	-0.44139900
	H	3.79215200	-1.54987700	-1.40060800
	H	3.65527400	-2.05400400	0.28393700
	C	3.33256100	1.03429000	-0.90851200
	H	3.79227600	1.98782100	-0.64157300
	H	3.65551700	0.78108500	-1.92060000
	Br	-3.46913200	-0.00000200	0.00004500
NBrSAC	Br	0.70228800	0.12162600	-0.09915000
	N	-1.24035100	0.13638700	-0.16831500
	C	-1.99263200	1.29219400	-0.09178600
	O	-1.56010900	2.41548000	-0.09935400
	N	3.02028900	0.09378800	-0.00484400
	C	3.58178400	0.78733600	-1.17932500
	H	3.26470200	1.83104600	-1.12541100
	H	3.13818900	0.34810400	-2.07503700
	C	5.13147800	0.63986300	-1.15255200
	H	5.47791500	-0.00177200	-1.96558900
	H	5.61893800	1.61024700	-1.26442400
	N	5.56149600	0.04038000	0.11308300
	C	5.02735200	-1.32124400	0.20079800
	H	5.29529100	-1.72717200	1.17859800
	H	5.51185800	-1.93757100	-0.55887700
	C	3.48304400	-1.30717000	0.00636700
	H	3.18150500	-1.75879400	-0.94114900
	H	2.95778600	-1.83054700	0.80775400
	C	3.47024400	0.76982000	1.22664300
	H	3.08278100	0.19839500	2.07281000
	H	3.01310100	1.76097400	1.25432800
	C	5.02549800	0.83403700	1.22174000
	H	5.37484700	1.86182200	1.10182100
	H	5.43590100	0.45068200	2.15788100
	C	-3.66371900	-0.44528600	0.03587800
	C	-3.44381100	0.91957500	-0.00133000
	C	-4.92674100	-1.00099400	0.11623300
	H	-5.07181100	-2.07375300	0.14153000
	C	-4.51349000	1.79935200	0.04541800
	H	-4.33302600	2.86706000	0.01584700
	C	-6.00115800	-0.11464500	0.16346600
	H	-7.00965200	-0.50456200	0.22778200
	C	-5.79702600	1.26602600	0.12850100
	H	-6.65209900	1.92986800	0.16613400
	O	-1.99052200	-2.07761100	-1.25447500
	S	-2.10708000	-1.30938900	-0.03568800
	O	-1.80287000	-1.95509300	1.22226700
BrCl	Br	1.60379400	0.00031800	0.00021100
	N	-0.70516700	0.00021000	0.00031400
	C	-1.19431500	-1.38365300	0.14248200
	C	-1.19514900	0.81529100	1.12728600
	C	-1.19445500	0.56874600	-1.26927700
	N	-3.24752100	-0.00040600	-0.00039100
	H	-0.71609700	-1.99118100	-0.62801600
	H	-0.85878400	-1.75019900	1.11473000
	H	-0.71740000	0.45204400	2.03901100
	H	-0.85972200	1.84061600	0.95870000

	H	-0.71687500	1.54015500	-1.40983700
	H	-0.85825600	-0.08968600	-2.07279000
	C	-2.74648300	-1.37682500	0.01664000
	H	-3.20829900	-1.90814700	0.85093000
	H	-3.06635700	-1.86493700	-0.90641500
	C	-2.74733000	0.70262300	1.18338300
	H	-3.20933400	1.69074400	1.22608000
	H	-3.06764000	0.14725500	2.06744500
	C	-2.74667500	0.67337200	-1.20081000
	H	-3.20802600	0.21639700	-2.07828000
	H	-3.06714900	1.71663100	-1.16199600
	Cl	3.88449300	-0.00039900	-0.00027200
BrF	Br	1.87684900	-0.00002900	0.00005700
	N	-0.33619100	-0.00007600	0.00002300
	C	-0.83065100	-0.41251200	-1.33073000
	C	-0.83072000	-0.94618400	1.02261900
	C	-0.83063300	1.35864900	0.30814000
	N	-2.88160400	0.00001600	-0.00003600
	H	-0.34970500	0.22217100	-2.07677500
	H	-0.49520300	-1.43809500	-1.49599000
	H	-0.34969900	-1.90959700	0.84605300
	H	-0.49536600	-0.57634600	1.99339900
	H	-0.34965100	1.68739000	1.23079400
	H	-0.49516000	2.01461700	-0.49738000
	C	-2.38113200	-0.28390100	-1.34663500
	H	-2.84425500	-1.20416800	-1.70712300
	H	-2.69878900	0.52794000	-2.00415400
	C	-2.38113900	-1.02427100	0.91914400
	H	-2.84426200	-0.87630000	1.89634300
	H	-2.69882800	-1.99967000	0.54498100
	C	-2.38117500	1.30823000	0.42738700
	H	-2.84419400	2.08057300	-0.18941100
	H	-2.69900400	1.47197500	1.45915600
	F	3.75685200	0.00009700	-0.00015100
DABCO-Br+[f]	N	2.13834100	0.00026600	-0.00017600
	N	4.67551900	-0.00046800	0.00005200
	C	2.63341400	-1.30050700	-0.52355800
	H	2.30821700	-1.37448500	-1.56269800
	H	2.15131000	-2.09595700	0.04632600
	C	4.18487600	-1.32152300	-0.38246900
	H	4.49299800	-2.03756600	0.38087200
	H	4.64872400	-1.61711100	-1.32409900
	C	2.63410500	1.10388800	-0.86477500
	H	2.30911600	2.04092100	-0.40935800
	H	2.15237300	1.00830900	-1.83881500
	C	4.18563300	0.99167000	-0.95282600
	H	4.49427900	0.68884200	-1.95454300
	H	4.64975100	1.95470800	-0.73741900
	C	2.63368000	0.19702500	1.38797700
	H	2.30817400	-0.66583400	1.97156500
	H	2.15194700	1.08837800	1.79215600
	C	4.18528000	0.32890500	1.33546400
	H	4.49415300	1.34769700	1.57426600
	H	4.64878000	-0.33934000	2.06196400
	Br	-0.00002100	0.00033900	0.00009100
	N	-2.13837500	-0.00001600	0.00005300

	N	-4.67547900	-0.00017200	-0.00011500
	C	-2.63387100	-0.40467600	1.34239700
	H	-2.30923200	0.36035200	2.04975800
	H	-2.15157500	-1.34657600	1.60736200
	C	-4.18528200	-0.52829500	1.26983900
	H	-4.49328900	-1.57181100	1.35079200
	H	-4.64953600	0.02130800	2.08933800
	C	-2.63379700	1.36482600	-0.32055100
	H	-2.30889000	1.59525300	-1.33661500
	H	-2.15169000	2.06504700	0.36300100
	C	-4.18530700	1.36378200	-0.17765500
	H	-4.49363800	1.95561200	0.68550100
	H	-4.64945400	1.79860200	-1.06346200
	C	-2.63359700	-0.96022500	-1.02168900
	H	-2.30850800	-1.95529500	-0.71306700
	H	-2.15135300	-0.71838800	-1.96983500
	C	-4.18507600	-0.83599600	-1.09246800
	H	-4.49314700	-0.38443100	-2.03669400
	H	-4.64917600	-1.82059400	-1.02629400
pyrazine-Br+[f]	N	-1.65583100	-0.00055200	0.00021300
	C	-2.15456900	1.40699300	-0.06613300
	C	-2.15552800	-0.76096800	-1.18602900
	C	-2.15622300	-0.64651000	1.25215200
	N	-4.19246300	0.00088500	-0.00060200
	H	-1.66529000	1.96944400	0.72936100
	H	-1.83554500	1.81152000	-1.02771000
	H	-1.66504900	-0.35443200	-2.07067000
	H	-1.83780000	-1.79640900	-1.05588500
	H	-1.66691200	-1.61646300	1.34269700
	H	-1.83727200	-0.01642300	2.08354200
	C	-3.70379900	1.37287400	0.08758500
	H	-4.17215300	1.97335100	-0.69261600
	H	-4.00283300	1.78522500	1.05215900
	C	-3.70452300	-0.60927200	-1.23307500
	H	-4.17415500	-1.58455400	-1.36306500
	H	-4.00303900	0.02021700	-2.07242200
	C	-3.70524200	-0.76191100	1.14397500
	H	-4.17445400	-0.38656700	2.05369900
	H	-4.00470100	-1.80325100	1.01822900
	Br	0.39020700	-0.00060400	0.00063400
	C	3.29725200	-1.14867400	0.00022400
	C	3.29635600	1.14857700	0.00017500
	C	4.68908200	-1.13395500	-0.00064200
	H	2.72405800	-2.06815700	0.00046300
	C	4.68817100	1.13498400	-0.00046400
	H	2.72245100	2.06763400	0.00029800
	H	5.24938600	-2.06188200	-0.00089100
	H	5.24771400	2.06336800	-0.00089100
	N	2.62406800	-0.00030600	0.00057300
	N	5.38029500	0.00078800	-0.00091200