Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Lone-pair–π interactions: analysis of the physical origin and biolological implications

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Electronic Supplementary Information

Fig. S1: Electrostatic (ES) and Orbital (ORB) components of the Cl^--TCB complex in the asymmetric chloride approach along the normale to the TCB ring through the N-atom ("off-center") and in the symmetrical approach along the C_2 axis towards the ring centroid ("sym"). EDA-DFT decomposition analysis using the ADF 16 program, M06-2X exchange-correlation functional, TZP2P basis set, scans without geometry relaxation. The arrows indicate the calculated equilibrium distances

Table S1: EDA-DFT energy decomposition analysis of the symmetrical Cl^--TCB complex. Conditions as in Fig. S1, but including geometry relaxation

Table S2: PDB coordinate files of the analyzed complexes

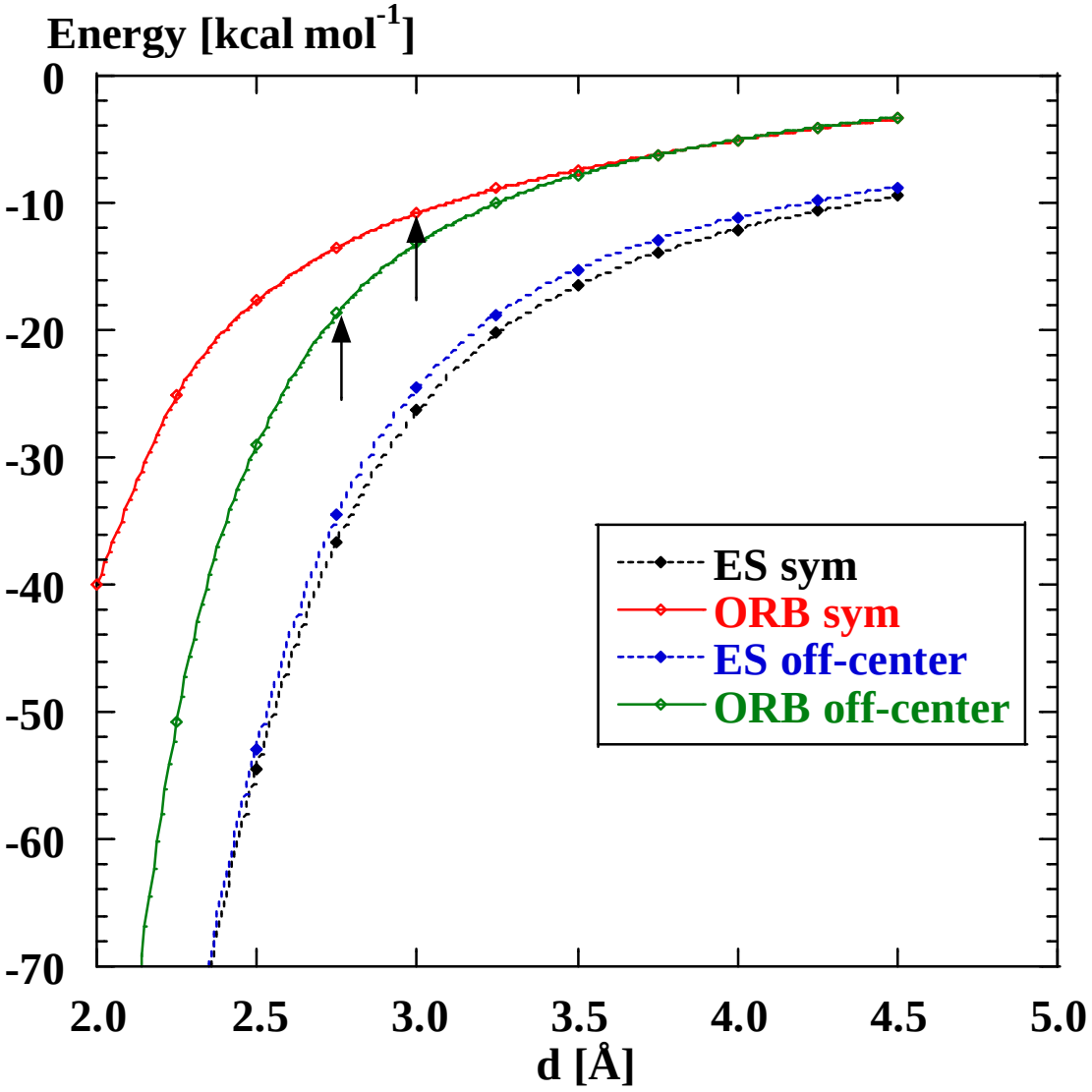

Fig. S1: Electrostatic (ES) and Orbital energy (ORB) components of the Cl^--TCB complex in the asymmetric chloride approach along the normale to the TCB ring through the C(H) atom ("off-center") and in the symmetrical approach along the C_2 axis towards the ring centroid ("sym"), as a function of distance from the ring plane. EDA-DFT decomposition analysis using the ADF 16 program, M06-2X exchange-correlation functional, TZP2P basis set, scans without geometry relaxation. The arrows indicate the calculated equilibrium distances

Table S1: Energy decomposition analysis of Cl^--TCB complex in the asymmetric chloride approach along the normale to the TCB ring through the C(H)-atom ("TCB-C(H)", entries from Table 1), and in the symmetrical approach along the C_2 axis towards the ring centroid ("TCB-M"). EDA-DFT decomposition analysis using the ADF 16 program, M06-2X exchange-correlation functional, TZP2P basis set.

	lp-donor →	**Cl^-**	
Method ↓	**arene →**	TCB-M lp···π	TCB-C(H) lp···π
	DI		**0.220**
EDA	**ES**	**-23.7**	**-33.8**
	PAULI	**5.9**	**23.0**
	ORB	**-9.7**	**-18.0**
	TOT[c]	**-27.6**	**-28.8**
	d_{X-Y} [Å][a]	**3.00**	**2.78**
	d_{X-Y}(vdW) [Å][b]	**-**	**3.45**

[a] closest atom-atom or atom-centroid distance between the fragments
[b] van der Waals radii taken from Bondi, [1], correction for H from Rowland and Taylor[2]
[c] Total interaction energy between fragments relaxed in the complex

1 A. Bondi, *J. Chem. Phys.*, 1964, **68**, 441.
2 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100,**, 7384.

Table S1: PDB coordinate files of the analyzed complexes

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COMPND    Indole-N-water (lp-π)
AUTHOR    GENERATED BY OPEN BABEL 2.3.90
HETATM    1  N   LIG     1      -1.271   1.200   0.060  1.00  0.00           N
HETATM    2  C   LIG     1      -0.955  -0.137  -1.736  1.00  0.00           C
HETATM    3  C   LIG     1       2.457  -0.601  -0.068  1.00  0.00           C
HETATM    4  C   LIG     1       0.968   0.874   1.195  1.00  0.00           C
HETATM    5  C   LIG     1      -1.860   0.669  -1.081  1.00  0.00           C
HETATM    6  C   LIG     1       0.249  -0.155  -0.944  1.00  0.00           C
HETATM    7  C   LIG     1       1.500  -0.791  -1.064  1.00  0.00           C
HETATM    8  C   LIG     1       2.192   0.219   1.053  1.00  0.00           C
HETATM    9  C   LIG     1       0.010   0.686   0.191  1.00  0.00           C
HETATM   10  H   LIG     1      -2.879   0.927  -1.340  1.00  0.00           H
HETATM   11  H   LIG     1      -1.790   1.626   0.815  1.00  0.00           H
HETATM   12  H   LIG     1       0.767   1.510   2.055  1.00  0.00           H
HETATM   13  H   LIG     1       2.958   0.346   1.815  1.00  0.00           H
HETATM   14  H   LIG     1       3.424  -1.091  -0.150  1.00  0.00           H
HETATM   15  H   LIG     1       1.715  -1.426  -1.922  1.00  0.00           H
HETATM   16  H   LIG     1      -1.123  -0.650  -2.674  1.00  0.00           H
HETATM   17  O   HOH     2      -2.297  -1.287   1.639  1.00  0.00           O
HETATM   18  H   HOH     2      -2.622  -1.975   1.036  1.00  0.00           H
HETATM   19  H   HOH     2      -1.573  -1.721   2.118  1.00  0.00           H

COMPND    Indole-N-water (OH-π)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  N   LIG     1      -1.305  -0.048  -1.127  1.00  0.00           N
HETATM    2  C   LIG     1      -0.979   1.674   0.299  1.00  0.00           C
HETATM    3  C   LIG     1       2.483   0.068   0.544  1.00  0.00           C
HETATM    4  C   LIG     1       0.992  -1.114  -0.995  1.00  0.00           C
HETATM    5  C   LIG     1      -1.894   1.069  -0.532  1.00  0.00           C
HETATM    6  C   LIG     1       0.240   0.909   0.231  1.00  0.00           C
HETATM    7  C   LIG     1       1.503   1.010   0.849  1.00  0.00           C
HETATM    8  C   LIG     1       2.231  -0.982  -0.368  1.00  0.00           C
HETATM    9  C   LIG     1       0.011  -0.163  -0.690  1.00  0.00           C
HETATM   10  H   LIG     1      -2.921   1.327  -0.751  1.00  0.00           H
HETATM   11  H   LIG     1      -1.741  -0.630  -1.829  1.00  0.00           H
HETATM   12  H   LIG     1       0.797  -1.927  -1.692  1.00  0.00           H
HETATM   13  H   LIG     1       3.017  -1.702  -0.583  1.00  0.00           H
HETATM   14  H   LIG     1       3.461   0.138   1.015  1.00  0.00           H
HETATM   15  H   LIG     1       1.707   1.815   1.553  1.00  0.00           H
HETATM   16  H   LIG     1      -1.161   2.552   0.906  1.00  0.00           H
HETATM   17  O   HOH     2      -2.295  -1.935   1.307  1.00  0.00           O
HETATM   18  H   HOH     2      -1.924  -1.268   0.704  1.00  0.00           H
HETATM   19  H   HOH     2      -1.620  -2.018   2.000  1.00  0.00           H

COMPND    Indole-NH-water(N-H··O)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  N   LIG     1      -1.318   0.219  -0.170  1.00  0.00           N
HETATM    2  C   LIG     1      -0.229   2.173   0.195  1.00  0.00           C
HETATM    3  C   LIG     1       2.790  -0.177   0.224  1.00  0.00           C
HETATM    4  C   LIG     1       0.668  -1.349  -0.106  1.00  0.00           C
HETATM    5  C   LIG     1      -1.465   1.590   0.018  1.00  0.00           C
HETATM    6  C   LIG     1       0.748   1.115   0.161  1.00  0.00           C
HETATM    7  C   LIG     1       2.151   1.060   0.288  1.00  0.00           C
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HETATM    8  C   LIG     1       2.056  -1.371   0.034  1.00  0.00           C
HETATM    9  C   LIG     1       0.026  -0.105  -0.043  1.00  0.00           C
HETATM   10  H   LIG     1      -2.449   2.040  -0.011  1.00  0.00           H
HETATM   11  H   LIG     1      -2.077  -0.458  -0.095  1.00  0.00           H
HETATM   12  H   LIG     1       0.104  -2.267  -0.259  1.00  0.00           H
HETATM   13  H   LIG     1       2.584  -2.321  -0.009  1.00  0.00           H
HETATM   14  H   LIG     1       3.872  -0.230   0.324  1.00  0.00           H
HETATM   15  H   LIG     1       2.726   1.972   0.437  1.00  0.00           H
HETATM   16  H   LIG     1      -0.038   3.230   0.328  1.00  0.00           H
HETATM   17  O   HOH     2      -3.545  -1.774   0.138  1.00  0.00           O
HETATM   18  H   HOH     2      -3.464  -2.241   0.986  1.00  0.00           H
HETATM   19  H   HOH     2      -3.502  -2.470  -0.538  1.00  0.00           H

COMPND    Indole-N-Cl⁻ (lp-π)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  N   LIG     1      -0.752   1.277  -0.733  1.00  0.00           N
HETATM    2  C   LIG     1      -0.202  -0.536  -1.962  1.00  0.00           C
HETATM    3  C   LIG     1       2.641  -0.688   0.593  1.00  0.00           C
HETATM    4  C   LIG     1       1.106   1.179   0.974  1.00  0.00           C
HETATM    5  C   LIG     1      -1.103   0.497  -1.821  1.00  0.00           C
HETATM    6  C   LIG     1       0.768  -0.397  -0.910  1.00  0.00           C
HETATM    7  C   LIG     1       1.917  -1.111  -0.522  1.00  0.00           C
HETATM    8  C   LIG     1       2.237   0.446   1.336  1.00  0.00           C
HETATM    9  C   LIG     1       0.390   0.763  -0.154  1.00  0.00           C
HETATM   10  H   LIG     1      -2.025   0.691  -2.351  1.00  0.00           H
HETATM   11  H   LIG     1      -1.375   1.941  -0.296  1.00  0.00           H
HETATM   12  H   LIG     1       0.769   2.026   1.568  1.00  0.00           H
HETATM   13  H   LIG     1       2.804   0.738   2.218  1.00  0.00           H
HETATM   14  H   LIG     1       3.523  -1.244   0.908  1.00  0.00           H
HETATM   15  H   LIG     1       2.226  -1.997  -1.076  1.00  0.00           H
HETATM   16  H   LIG     1      -0.239  -1.314  -2.715  1.00  0.00           H
HETATM   17 CL   LIG     2      -2.582  -0.576   1.204  1.00  0.00          Cl

COMPND    Uracil-N-water (lp-π)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  N   LIG     1      -0.063  -0.220   0.946  1.00  0.00           N
HETATM    2  C   LIG     1      -1.352  -0.009   0.388  1.00  0.00           C
HETATM    3  C   LIG     1      -1.380   1.040  -0.626  1.00  0.00           C
HETATM    4  C   LIG     1      -0.223   1.612  -1.039  1.00  0.00           C
HETATM    5  N   LIG     1       0.996   1.255  -0.504  1.00  0.00           N
HETATM    6  C   LIG     1       1.150   0.273   0.487  1.00  0.00           C
HETATM    7  O   LIG     1      -2.310  -0.671   0.777  1.00  0.00           O
HETATM    8  H   LIG     1      -2.335   1.309  -1.060  1.00  0.00           H
HETATM    9  H   LIG     1      -0.186   2.375  -1.813  1.00  0.00           H
HETATM   10  H   LIG     1       1.861   1.642  -0.862  1.00  0.00           H
HETATM   11  O   LIG     1       2.246  -0.082   0.900  1.00  0.00           O
HETATM   12  H   LIG     1       0.008  -0.989   1.608  1.00  0.00           H
HETATM   13  O   HOH     2       0.515  -2.314  -1.220  1.00  0.00           O
HETATM   14  H   HOH     2       1.312  -2.824  -1.002  1.00  0.00           H
HETATM   15  H   HOH     2      -0.198  -2.971  -1.258  1.00  0.00           H

COMPND    Uracil-M-water (lp-π)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  N   LIG     1       0.599  -1.171  -0.064  1.00  0.00           N
HETATM    2  C   LIG     1       1.404   0.000  -0.083  1.00  0.00           C
HETATM    3  C   LIG     1       0.631   1.235  -0.099  1.00  0.00           C
HETATM    4  C   LIG     1      -0.721   1.190  -0.001  1.00  0.00           C
HETATM    5  N   LIG     1      -1.404   0.000   0.083  1.00  0.00           N
HETATM    6  C   LIG     1      -0.780  -1.254   0.102  1.00  0.00           C
HETATM    7  O   LIG     1       2.630  -0.095  -0.083  1.00  0.00           O
HETATM    8  H   LIG     1       1.166   2.175  -0.159  1.00  0.00           H
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HETATM    9  H   LIG     1      -1.338   2.084   0.025  1.00  0.00           H
HETATM   10  H   LIG     1      -2.406  -0.018   0.237  1.00  0.00           H
HETATM   11  O   LIG     1      -1.397  -2.302   0.241  1.00  0.00           O
HETATM   12  H   LIG     1       1.097  -2.058  -0.043  1.00  0.00           H
HETATM   13  O   HOH     2       0.000   0.000   3.084  1.00  0.00           O
HETATM   14  H   HOH     2      -0.220  -0.880   3.428  1.00  0.00           H
HETATM   15  H   HOH     2       0.894   0.165   3.424  1.00  0.00           H

COMPND    TCB-CH-water (lp-π)
AUTHOR    GENERATED BY OPEN BABEL 2.2.3
HETATM    1  C   LIG     1       2.408   1.764  -0.173  1.00  0.00           C
HETATM    2  C   LIG     1       1.205   0.997  -0.260  1.00  0.00           C
HETATM    3  C   LIG     1       2.504  -1.100  -0.520  1.00  0.00           C
HETATM    4  C   LIG     1       1.254  -0.412  -0.443  1.00  0.00           C
HETATM    5  C   LIG     1      -0.036   1.640  -0.152  1.00  0.00           C
HETATM    6  C   LIG     1      -1.228   0.906  -0.219  1.00  0.00           C
HETATM    7  C   LIG     1       0.062  -1.143  -0.521  1.00  0.00           C
HETATM    8  C   LIG     1      -1.178  -0.503  -0.401  1.00  0.00           C
HETATM    9  C   LIG     1      -2.481   1.581  -0.092  1.00  0.00           C
HETATM   10  C   LIG     1      -2.374  -1.282  -0.435  1.00  0.00           C
HETATM   11  H   LIG     1      -0.073   2.715  -0.011  1.00  0.00           H
HETATM   12  H   LIG     1       0.100  -2.219  -0.650  1.00  0.00           H
HETATM   13  N   LIG     1      -3.494   2.145   0.013  1.00  0.00           N
HETATM   14  N   LIG     1       3.380   2.401  -0.101  1.00  0.00           N
HETATM   15  N   LIG     1       3.510  -1.683  -0.570  1.00  0.00           N
HETATM   16  N   LIG     1      -3.335  -1.940  -0.449  1.00  0.00           N
HETATM   17  O   HOH     2       0.108  -1.467   2.538  1.00  0.00           O
HETATM   18  H   HOH     2       0.902  -1.946   2.828  1.00  0.00           H
HETATM   19  H   HOH     2      -0.634  -2.014   2.844  1.00  0.00           H

COMPND    TCB-CH-Cl- (lp-π)  Cl constrained to lie on the normal through C(H)
ATOM      1  C         X   1      -1.219   1.030  -0.076  0.00  0.00           C
ATOM      2  C         X   1      -1.222  -0.297  -0.579  0.00  0.00           C
ATOM      3  C         X   1       0.000  -0.957  -0.815  0.00  0.00           C
ATOM      4  C         X   1       1.222  -0.297  -0.579  0.00  0.00           C
ATOM      5  C         X   1       1.219   1.030  -0.076  0.00  0.00           C
ATOM      6  C         X   1      -0.000   1.674   0.190  0.00  0.00           C
ATOM      7  H         X   1       0.000  -1.971  -1.193  0.00  0.00           H
ATOM      8  H         X   1      -0.000   2.684   0.585  0.00  0.00           H
ATOM      9  C         X   1       2.447  -0.964  -0.876  0.00  0.00           C
ATOM     10  N         X   1       3.442  -1.501  -1.161  0.00  0.00           N
ATOM     11  C         X   1       2.439   1.729   0.171  0.00  0.00           C
ATOM     12  N         X   1       3.417   2.331   0.368  0.00  0.00           N
ATOM     13  C         X   1      -2.439   1.729   0.170  0.00  0.00           C
ATOM     14  N         X   1      -3.417   2.331   0.367  0.00  0.00           N
ATOM     15  C         X   1      -2.447  -0.964  -0.875  0.00  0.00           C
ATOM     16  N         X   1      -3.442  -1.501  -1.160  0.00  0.00           N
ATOM     17  Cl        X   1       0.000  -1.895   1.803  0.00  0.00          CL

COMPND    TCB-CH-Cl- (lp-π)  fully optimized
ATOM      1  C         X   1      -1.217   1.053  -0.063  0.00  0.00           C
ATOM      2  C         X   1      -1.224  -0.289  -0.518  0.00  0.00           C
ATOM      3  C         X   1       0.000  -1.003  -0.623  0.00  0.00           C
ATOM      4  C         X   1       1.224  -0.288  -0.518  0.00  0.00           C
ATOM      5  C         X   1       1.217   1.053  -0.063  0.00  0.00           C
ATOM      6  C         X   1      -0.000   1.706   0.198  0.00  0.00           C
ATOM      7  H         X   1       0.000  -1.996  -1.047  0.00  0.00           H
ATOM      8  H         X   1      -0.000   2.729   0.556  0.00  0.00           H
ATOM      9  C         X   1       2.446  -0.941  -0.848  0.00  0.00           C
ATOM     10  N         X   1       3.440  -1.464  -1.159  0.00  0.00           N
ATOM     11  C         X   1       2.437   1.774   0.121  0.00  0.00           C
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ATOM     12  N       X   1       3.412   2.395   0.273  0.00  0.00           N
ATOM     13  C       X   1      -2.437   1.775   0.120  0.00  0.00           C
ATOM     14  N       X   1      -3.412   2.395   0.271  0.00  0.00           N
ATOM     15  C       X   1      -2.446  -0.941  -0.847  0.00  0.00           C
ATOM     16  N       X   1      -3.441  -1.465  -1.158  0.00  0.00           N
ATOM     17  Cl      X   1       0.000  -2.304   1.568  0.00  0.00          CL
END
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