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

SUPPORTING INFORMATION:

Effects of Steric Interactions on the Relativistic Spin-Orbit and Paramagnetic Components of the ^{13}C NMR Shielding Tensors of Di-haloethenes

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Comparative Analyses of Basis Function and Inclusion of the Solvent Model between theoretical data of ^{13}C NMR chemical shifts obtained for *cis*- and *trans*-1,2-dihaloethenes.

Table 1S. Theoretical ^{13}C NMR chemical shifts (δ_{theo}) and shielding tensors for each PAS coordinate (σ_{11}, σ_{22} and σ_{33}) for *cis*- and *trans*-1,2-diiodoethenes calculated with different combinations of basis/solvent model.

Method	δ_{theo}			σ_{11}			σ_{22}			σ_{33}		
	cis	***trans***	**Δ^a**	***cis***	***trans***	**Δ^b**	***cis***	***trans***	**Δ^b**	***cis***	***trans***	**Δ^b**
TZ2P	104.9	82.7	**22.2**	-16.7	8.0	**-24.7**	129.6	141.1	**-11.5**	157.0	187.5	**-30.5**
TZ2P/COSMO	106.7	84.9	**21.8**	-19.0	5.5	**-24.5**	126.7	137.8	**-11.1**	156.6	187.3	**-30.7**
QZ4P	110.0	87.6	**22.4**	-28.7	-2.8	**-25.9**	118.8	129.6	**-10.8**	149.0	180.8	**-31.8**
QZ4P/COSMO	112.5	90.1	**22.4**	-30.6	-5.2	**-25.4**	116.4	126.9	**-10.5**	148.8	180.5	**-31.7**

[a] $\Delta = \delta_{cis} - \delta_{trans}$. [b] $\Delta = \sigma_{cis} - \sigma_{trans}$.

Experimental and theoretical data of ^{13}C NMR chemical shifts obtained for *cis*- and *trans*-1,2-dihaloethenes with different DFT methods (B3LYP, PBE0 and BP86).

Table 2S. The experimental (δ_{exp}) and theoretical (δ_{theo}[a,b]) ^{13}C NMR chemical shift, the nuclear shielding tensor (σ_{total}[c]) and the diamagnetic (σ_{dia}), paramagnetic (σ_{para}) and spin-orbit (σ_{so}) components obtained for *cis*- and *trans*-1,2-dihaloethenes, calculated at the B3LYP/TZ2P level and using the SO-ZORA Hamiltonian.

	cis						***trans***					
	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}
F	238.1	-202.5	1.3	36.8	149.6	138.5[d]	237.1	-211.1	1.2	27.2	159.2	146.8[d]
Cl	246.2	-198.4	3.6	51.4	135.0	120.8	242.5	-194.5	3.8	51.8	134.6	120.3
Br	243.2	-199.7	14.6	58.0	128.4	113.6	239.4	-191.0	16.7	65.0	121.5	107.3
I	243.6	-200.0	33.6	76.4	110.0	97.8	243.6	-188.8	41.5	95.6	90.8	80.4

[a] $\delta_{theo} = \sigma_{TMS} - \sigma_{total}$. [b] The TMS shielding tensor is 186.4 ppm for respective level of theory. [c] $\sigma_{total} = \sigma_{dia} + \sigma_{para} + \sigma_{SO}$. [d] Experimental values were taken from ref. 46.

Table 3S. The experimental (δ_{exp}) and theoretical (δ_{theo}[a,b]) ^{13}C NMR chemical shift, the nuclear shielding tensor (σ_{total}[c]) and the diamagnetic (σ_{dia}), paramagnetic (σ_{para}) and spin-orbit (σ_{so}) components obtained for *cis*- and *trans*-1,2-dihaloethenes, calculated at the PBE0/TZ2P level and using the SO-ZORA Hamiltonian.

	cis						***trans***					
	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}
F	237.8	-194.0	1.3	45.2	146.7	138.5[d]	236.9	-202.6	1.2	35.5	156.4	146.8[d]
Cl	246.4	-190.3	3.4	59.5	132.4	120.8	242.6	-186.6	3.6	59.6	132.3	120.3
Br	242.9	-191.2	13.6	65.2	126.7	113.6	238.8	-183.1	15.5	71.2	120.7	107.3
I	242.7	-191.3	30.9	81.6	110.3	97.8	242.9	-181.7	38.5	99.2	92.7	80.4

[a] $\delta_{theo} = \sigma_{TMS} - \sigma_{total}$. [b] TMS shielding tensor is 191.9 ppm for respective level of theory. [c] $\sigma_{total} = \sigma_{dia} + \sigma_{para} + \sigma_{SO}$. [d] Experimental values were taken from ref. 46.

Table 4S. The experimental (δ_{exp}) and theoretical (δ_{theo}[a,b]) ^{13}C NMR chemical shift, the nuclear shielding tensor (σ_{total}[c]) and the diamagnetic (σ_{dia}), paramagnetic (σ_{para}) and spin-orbit (σ_{so}) components obtained for *cis*- and *trans*-1,2-dihaloethenes, calculated at the BP86/TZ2P level and using the SO-ZORA Hamiltonian.

	cis						***trans***					
	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}	σ_{dia}	σ_{para}	σ_{SO}	σ_{total}	δ_{theo}	δ_{exp}
F	237.2	-200.4	1.3	38.1	146.7	138.5[d]	237.3	-209.6	1.2	28.8	156.0	146.8[d]
Cl	244.8	-194.0	3.4	54.2	130.6	120.8	244.5	-194.0	3.6	54.0	130.8	120.3
Br	241.8	-195.4	13.3	59.6	125.2	113.6	241.5	-190.7	15.7	66.5	118.4	107.3
I	243.6	-197.5	29.1	74.5	110.3	97.8	243.8	-186.0	38.3	95.4	89.4	80.4

[a] $\delta_{theo} = \sigma_{TMS} - \sigma_{total}$. [b] TMS shielding tensor is 184.8 ppm for respective level of theory. [c] $\sigma_{total} = \sigma_{dia} + \sigma_{para} + \sigma_{SO}$. [d] Experimental values were taken from ref. 46.

Analyses of the effect of numerical integration based on Voronoi method for the *cis*- and *trans*-1,2-diiodoethenes.

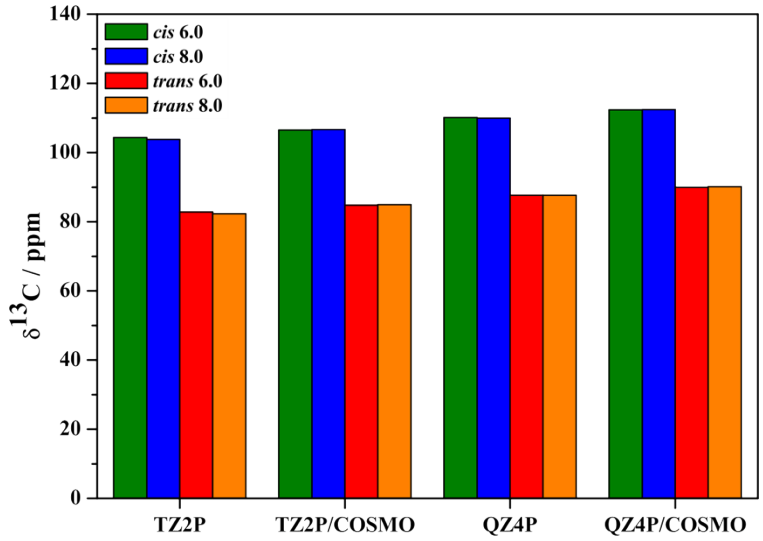

Figure 1S. Calculated ^{13}C NMR chemical shifts for *cis*- and *trans*-1,2-diiodoethene using the KT2/SO-ZORA level of theory with the TZ2P or QZ4P basis set, with and without the COSMO-RS solvent model. Each bar represents a numerical integration parameter used: 6.0 or 8.0. Geometry optimizations and SCF calculations were performed with the same integration parameter.

Graphical representations of the ^{13}C NMR shielding tensor for the *cis*- and *trans*-1,2-dihaloethenes (halo = F, Cl and Br).

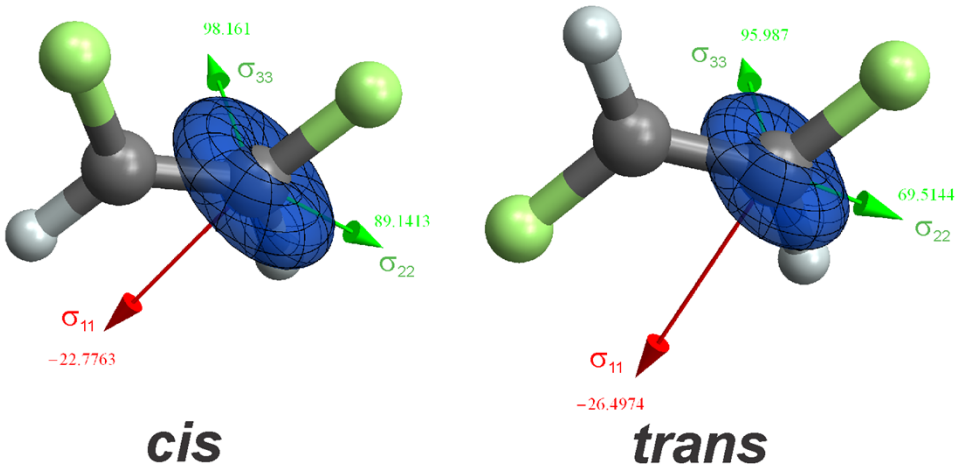

Figure 2S. Graphical representations of ^{13}C NMR shielding tensor for *cis*- and *trans*-difluoroethene. The arrows display the signs of the shielding tensor (red for negative terms and green for positive ones), and the surface indicates the magnitude of the shielding for a magnetic field in the direction of the carbon nucleus to a point on the surface via its distance from the carbon (polar plot).

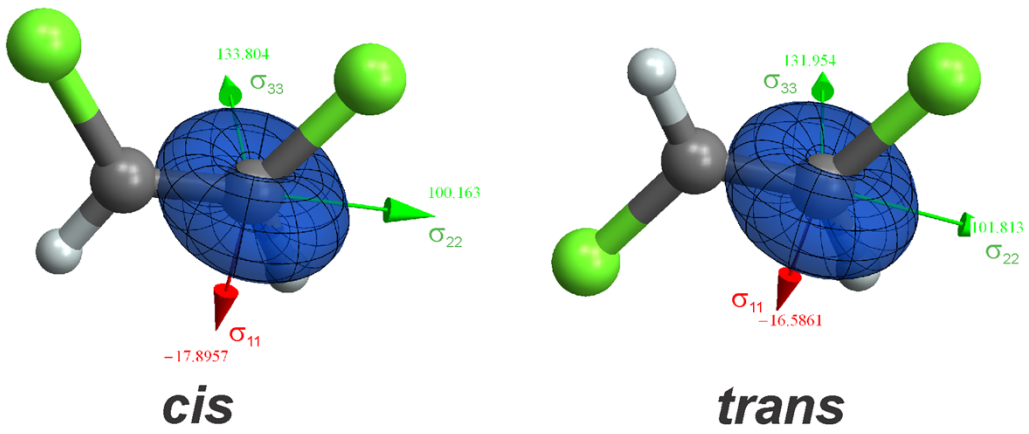

Figure 3S. Graphical representations of ^{13}C NMR shielding tensor for *cis*- and *trans*-dichloroethene. The arrows display the signs of the shielding tensor (red for negative terms and green for positive ones), and the surface indicates the magnitude of the shielding for a magnetic field in the direction of the carbon nucleus to a point on the surface via its distance from the carbon (polar plot).

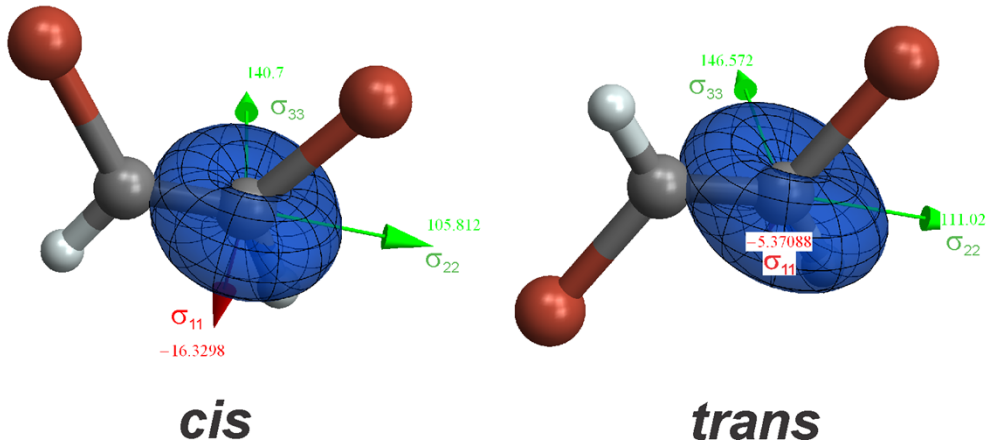

Figure 4S. Graphical representations of ^{13}C NMR shielding tensor for *cis*- and *trans*-dibromoethene. The arrows display the signs of the shielding tensor (red for negative terms and green for positive ones), and the surface indicates the magnitude of the shielding for a magnetic field in the direction of the carbon nucleus to a point on the surface via its distance from the carbon (polar plot).

Relevant NBO contributions for the ^{13}C NMR shielding tensor for each PAS orientation for *cis*- and *trans*-1,2-dihaloethenes.

Table 5S. Relevant NBO contributions (in ppm) for the paramagnetic (σ_{para}) and spin-orbit (σ_{SO}) components of the ^{13}C NMR shielding tensor for each PAS orientation for *cis*- and *trans*-1,2-dihaloethenes, calculated at the KT2/TZ2P level and using the SO-ZORA Hamiltonian. X_α means the halogen directly bonded to ^{13}C of the shielding tensor calculated and the X_β is associated with the neighbour carbon atom.

			NBO																			
			σ_{C-C}		$\pi_{C=C}$		$\sigma_{C\alpha-H}$		$\sigma_{C\alpha-X}$		$\sigma_{C\beta-H}$		$\sigma_{C\beta-X}$		σ^*_{C-C}		$\pi^*_{C=C}$		$\sigma^*_{C\alpha-H}$		$\sigma^*_{C\alpha-X}$	
			cis	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***
		σ_{11}	-131.5	-152.6	-56.0	-42.0	-7.6	-33.9	-54.1	-30.5	-13.4	-6.3	-1.3	-5.9	0.1	-0.5	-5.6	-0.3	0.5	2.4	9.3	3.6
F	σ_{para}	σ_{22}	-25.0	-6.9	-15.1	-42.8	-107.2	-92.1	-23.4	-42.0	-2.0	-10.6	-9.3	-3.6	-0.1	-0.0	1.1	-3.4	10.8	11.3	5.9	7.1
		σ_{33}	-49.7	-50.9	-0.11	-0.17	-44.9	-45.9	-15.6	-14.1	-2.7	-1.5	-0.1	0.3	-3.4	-4.4	0.1	-0.1	0.1	0.2	5.2	5.1
		σ_{11}	-149.5	-149.5	-14.1	-14.1	-32.7	-32.7	-44.4	-44.4	-11.9	-11.9	-8.8	-8.8	0.8	0.8	-6.7	-6.7	2.7	2.7	4.3	4.3
Cl	σ_{para}	σ_{22}	-1.0	-1.0	-3.2	-3.2	-92.8	-92.8	-70.6	-70.6	-10.3	-10.3	-16.3	-16.3	-0.1	-0.1	-8.8	-8.8	14.0	14.0	15.8	15.8
		σ_{33}	-40.2	-40.2	0.0	0.0	-33.2	-33.2	-9.2	-9.2	-2.5	-2.5	-2.1	-2.1	-8.2	-8.2	0.1	0.1	-3.6	-3.6	3.2	3.2
Br	σ_{para}	σ_{11}	-146.2	-147.0	-8.16	-7.8	-35.9	-56.1	-49.2	-28.6	-11.9	-12.9	-10.4	-10.2	0.4	-0.1	-11.8	-2.7	2.6	1.7	3.7	6.2

		σ_{22}	-0.8	-0.1	4.6	9.2	-92.6	-76.6	-85.4	-100.6	-11.9	-11.3	-19.1	-19.7	-0.2	0.0	-12.6	-15.2	16.0	15.1	19.6	17.7
		σ_{33}	-42.8	-43.4	0.1	0.0	-32.0	-34.0	-9.2	-7.2	-2.5	-5.8	-4.8	-1.5	-12.0	-10.8	0.0	-0.2	-2.7	-4.2	3.3	11.2
		σ_{11}	-0.8	1.6	0.8	1.1	-8.1	-10.2	10.7	9.8	1.8	-1.9	-1.9	2.5	2.4	2.9	1.5	1.0	-0.0	-0.2	0.8	0.8
	σ_{SO}	σ_{22}	1.0	-1.8	0.0	0.1	8.8	10.4	-7.3	-5.8	-1.6	1.8	2.0	-1.7	-0.3	-0.3	-3.3	-2.5	0.7	0.4	7.4	8.8
		σ_{33}	-0.7	-0.3	-1.1	-1.6	1.3	-0.4	2.5	3.5	0.2	0.2	-0.5	0.1	-1.4	0.6	0.5	0.4	2.2	3.0	7.8	10.2
		σ_{11}	-145.0	-144.2	-4.2	-0.8	-45.8	-54.7	-44.7	-34.2	-10.6	-13.6	-15.6	-12.4	0.7	0.6	-15.6	-4.9	4.2	0.8	2.4	7.9
	σ_{para}	σ_{22}	0.0	-0.2	25.3	31.1	-89.5	-79.7	-114.2	-121.4	-15.7	-12.6	-21.1	-26.1	0.1	0.0	-20.4	-20.9	18.6	18.4	25.2	22.6
		σ_{33}	-40.9	-40.5	0.1	0.1	-30.3	-33.1	-9.3	-7.1	-2.4	-8.8	-8.7	-1.4	-17.6	-14.1	-0.0	-0.2	-2.1	-5.5	1.7	14.2
I		σ_{11}	5.0	9.7	-1.7	-1.7	-21.8	-27.9	24.3	25.7	4.5	-5.5	-5.9	7.6	4.0	6.5	4.5	4.0	1.3	1.1	-3.3	-4.6
	σ_{SO}	σ_{22}	-4.8	-10.5	4.2	5.1	22.1	27.0	-15.7	-15.1	-4.3	5.4	6.3	-5.5	1.8	1.2	-9.0	-7.7	1.5	0.3	19.7	26.1
		σ_{33}	-3.0	-1.2	-3.4	-4.5	4.1	-1.9	6.5	10.9	0.2	0.3	-1.8	-0.0	-7.7	1.7	1.9	1.5	2.7	7.7	19.0	23.6

NLMO contributions of the halogen lone pairs for the ^{13}C NMR shielding tensor for each PAS orientation for *cis*- and *trans*-1,2-dihaloethenes.

Table 6S. NLMO contributions (in ppm) of the halogen *lone pairs* (LP) for the paramagnetic (σ_{para}) and spin-orbit (σ_{SO}) components of the ^{13}C NMR shielding tensor for each PAS orientation for *cis*- and *trans*-1,2-dihaloethenes, calculated at the KT2/TZ2P level and using the SO-ZORA Hamiltonian. X_α means the halogen directly bonded to ^{13}C of the shielding tensor calculated and the X_β is associated with the neighbour carbon atom.

	$LP_1(X_\alpha)$		**$LP_2(X_\alpha)$**		**$LP_3(X_\alpha)$**		**$LP_1(X_\beta)$**		**$LP_2(X_\beta)$**		**$LP_3(X_\beta)$**	
	cis	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***	***cis***	***trans***

		σ_{11}	-9.7	-5.4	0.2	1.3	-2.6	-0.7	-0.1	-0.1	-6.4	-4.4	-2.5	-0.5
F	σ_{para}	σ_{22}	-4.5	-7.6	2.0	0.8	0.7	-1.0	0.4	0.7	-0.2	-1.3	-0.6	-2.5
		σ_{33}	-8.4	-7.7	-3.1	-2.8	-1.0	-1.2	-0.4	-0.5	-1.0	-1.3	-0.2	-0.3
		σ_{11}	-3.7	-3.6	-1.2	-1.2	-3.6	-3.5	-0.2	-0.2	-6.7	-6.8	-0.9	-0.8
Cl	σ_{para}	σ_{22}	-8.7	-8.6	0.5	0.4	-6.3	-6.1	1.1	1.0	1.2	1.1	2.0	2.0
		σ_{33}	-5.2	-5.0	-2.8	-2.8	-0.9	-1.0	-0.3	-0.3	-4.1	-4.0	-0.1	-0.1
		σ_{11}	-2.9	-1.4	-2.1	-1.6	-4.4	-1.4	-0.2	-0.0	-5.5	-3.5	-2.6	0.3
	σ_{para}	σ_{22}	-8.7	-9.7	0.3	-0.3	-7.2	-8.6	1.3	1.2	1.6	-0.6	3.5	5.8
		σ_{33}	-4.1	-4.4	-0.1	0.7	-0.7	-1.2	-0.4	-0.6	-6.0	-2.8	-0.1	-0.5
Br		σ_{11}	0.8	0.4	0.6	0.4	0.9	0.8	-0.0	-0.0	-0.2	0.7	-0.2	-0.5
	σ_{SO}	σ_{22}	0.4	0.8	-0.5	-0.3	-1.3	-1.2	0.0	-0.0	0.3	-0.7	-0.0	0.5
		σ_{33}	1.5	1.7	-0.4	-0.3	1.1	0.4	-0.0	-0.0	-1.2	0.7	-0.3	-0.5

		σ_{11}	-2.1	-1.2	-2.5	-2.3	-4.5	-2.1	-0.2	-0.0	-4.2	-2.7	-5.0	0.5
	σ_{para}	σ_{22}	-9.4	-10.1	-0.1	-0.5	-11.2	-11.2	1.4	1.3	2.7	-0.6	6.9	9.9
		σ_{33}	-3.4	-3.8	2.8	3.2	-0.7	-1.2	-0.4	-0.7	-10.2	-2.8	-0.0	-0.5
I		σ_{11}	1.0	-0.1	1.4	1.2	2.4	2.2	-0.0	0.1	-1.0	2.7	-0.4	-1.2
	σ_{SO}	σ_{22}	1.7	2.7	-1.4	-0.9	-3.4	-3.1	-0.0	-0.2	0.9	-3.0	0.3	1.5
		σ_{33}	3.6	4.4	-1.3	-0.7	1.1	1.1	-0.0	-0.0	-7.0	1.0	-1.1	-1.5

NBO results for *cis*- and *trans*-1,2-dihaloethenes.

Table 7S. NBO occupancies[a] obtained using the scalar ZORA Hamiltonian and the KT2/TZ2P functional for *cis*- and *trans*-1,2-dihaloethenes.

	cis				***trans***			
NBO	**F**	**Cl**	**Br**	**I**	**F**	**Cl**	**Br**	**I**
LP_1X	1992.8	1994.1	1994.6	1993.9	1993.3	1994.7	1995.5	1995.4
LP_2X	1963.0	1964.1	1969.2	1968.8	1963.3	1962.3	1966.0	1964.5
LP_3X	1916.2	1901.0	1911.7	1914.4	1922.5	1913.3	1925.0	1928.3
σ_{C-X}	1995.9	1990.8	1986.7	1982.4	1993.1	1982.8	1973.3	1962.4
σ^*_{C-X}	17.6	23.9	31.4	38.6	15.4	24.7	36.0	47.6
σ_{C-H}	1980.6	1973.6	1969.4	1966.1	1986.8	1984.8	1983.7	1982.7
σ^*_{C-H}	23.6	23.0	20.8	21.0	24.0	23.0	20.4	20.5
σ_{C-C}	1996.2	1996.1	1996.6	1996.4	1996.9	1996.1	1996.3	1996.2
σ^*_{C-C}	30.5	34.4	30.8	30.9	24.9	26.4	23.2	23.7
$\pi_{C=C}$	1995.3	1987.4	1989.7	1988.9	1997.0	1988.0	1990.0	1988.9
$\pi^*_{C=C}$	156.5	191.1	170.4	164.3	144.9	167.7	144.7	137.3

[a] Occupancies are given in units of 10^{-3}.

Table 8S. NBO energies[a] obtained using the scalar ZORA Hamiltonian and the KT2/TZ2P functional for *cis*- and *trans*-1,2-dihaloethenes.

	cis				***trans***			
NBO	**F**	**Cl**	**Br**	**I**	**F**	**Cl**	**Br**	**I**
LP_1X	-1.0179	-0.8308	-0.8754	-0.8238	-1.0242	-0.8346	-0.8747	-0.8156
LP_2X	-0.3735	-0.2996	-0.2817	-0.2561	-0.3760	-0.3056	-0.2910	-0.2718
LP_3X	-0.3733	-0.2943	-0.2698	-0.2474	-0.3751	-0.2986	-0.2735	-0.2502
σ_{C-X}	-0.9205	-0.6829	-0.6097	-0.5528	-0.9106	-0.6760	-0.5997	-0.5438
σ^*_{C-X}	0.2060	0.1138	0.0548	0.0175	0.2001	0.1041	0.0431	0.0071
σ_{C-H}	-0.5264	-0.5258	-0.5220	-0.5205	-0.5288	-0.5303	-0.5285	-0.5287
σ^*_{C-H}	0.3879	0.3886	0.3956	0.4093	0.3864	0.3903	0.4008	0.4117
σ_{C-C}	-0.7348	-0.7501	-0.7527	-0.7568	-0.7367	-0.7550	-0.7592	-0.7654
σ^*_{C-C}	0.5295	0.4902	0.4933	0.4955	0.5312	0.4937	0.4974	0.4972
$\pi_{C=C}$	-0.2855	-0.2908	-0.2868	-0.2866	-0.2861	-0.2933	-0.2897	-0.2908
$\pi^*_{C=C}$	-0.0283	-0.0440	-0.0388	-0.0375	-0.0292	-0.0456	-0.0402	-0.0392

[a] Energies are given in au.

Energies of frontier MOs for *cis*- and *trans*-1,2-diiodoethenes with different C=C-I bond angles.

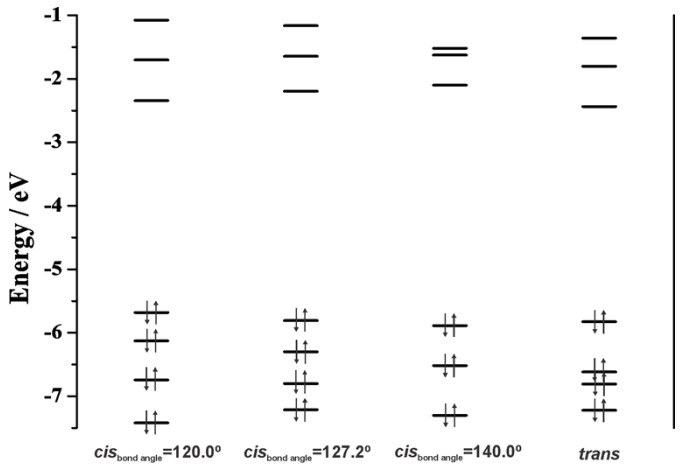

Figure 5S. Energies of frontier MOs for *cis*- and *trans*-diiodoethene calculated at the KT2/TZ2P level. It shows the values of energy for *cis* isomer with different C=C-I bond angles: equilibrium bond angle (127.2º) and bond angles equal to 120º and 140º.