Supplementary Material (ESI) for PCCP

Dimerisation of Nitrile Oxides: a Quantum-chemical Study

Supplementary Information

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Table S1: Total and relative energies of selected fluoro derivatives

	MRCI(2,2)		**MRCI(2,2)+DA**		**MR-AQCC(2,2)**		**MRCI(4,4)**		**MRCI(4,4)+DA**		**MR-AQCC(4,4)**	
	Total energy	ΔG	Total energy	ΔG	Total energy	ΔG	Total energy	ΔG	Total energy	ΔG	Total energy	ΔG
2 FCNO	---	---	---	---	2(-267.280205)	119	---	---	---	---	2(-267.282794)	97
ctc	-534.314265	0	-534.569814	0	-534.627587	0	-534.332512	0	-534.580220	0	-534.624234	0.0
TS2	.3001833	35	.557781	40	.616424	28	.318418	35	.568169	30	.613260	27
ttc	.317331	-8	.571730	-5	.628540	-2	.335265	-7	.581804	-4	.625413	-3
TS5	.309642	15	.564997	16	.621988	18	.328556	13	.575494	15	.620052	14
tcc	.318680	-11	.573058	-16	.629590	-5	.336765	-11	.583150	-7	.626654	-6
TS9	.322998	-18	.580417	-23	.637930	-22	.341580	-19	.590975	-23	.635422	-24
fur	.355315	-94	.615065	-105	.668079	-92	.371586	-89	.622953	-98	.663796	-90

[a] Total energies are in atomic units and relative Gibbs energies are in kJ/mol. Calculated using the 6-311+G(2d) basis set. Geometries, ZPE, and thermal corrections are calculated at the UB3LYP/6-311+G(d) level. Valence electrons were included in the correlation energy calculations ("fc").

Table S2: Total energies (in atomic units) of the minima and transition states of the lowest energy TS5 dimerisation routes of Nitrile Oxides to Furoxans[a]

	FCNO	**ClCNO**	**BrCNO**	**CH_3CNO**	**NCCNO**
XCNO	-267.36529	-627.38831	-2740.30799	-207.52588	-260.34694
TS1	----	-1254.76408	-5480.59917	-415.02779	-520.66351
ctc	-534.80422	-1254.80412	-5480.63327	-415.05665	-520.69592
TS2	-534.79312	-1254.79538	-5480.62559	-415.04143	-520.68149
ttc	-534.80433	-1254.80704	-5480.63660	-415.05502	-520.69369
TS5	-534.79697	-1254.80284	-5480.63332	-415.04525	-520.68865
fur	-534.84724	-1254.85487	-5480.68731	-415.10869	-520.74377

[a] Calculated at the MR-AQCC(2,2)//UB3LYP/cc-pVTZ level. Total energies of monomers are calculated at the SR-AQCC//B3LYP/cc-pVTZ level.

Table S3: Total energies (in atomic units) of the minima and transition states of the dimerisation routes of Nitrile Oxides to 1,2,4-oxadiazole-4-oxides (SP1) and 1,4,2,5-dioxadiazines (SP2)[a]

	FCNO	**ClCNO**	**BrCNO**	**CH_3CNO**	**NCCNO**
XCNO	-267.36611 (.41103)	-627.39130 (.43404)	-2740.36983 (.41326)	-207.52950 (.56891)	-260.35009 (.40566)
TSs1	-534.70210 (.79953)	-1254.74035 (.83715)	-5480.69333 (.79180)	-415.01372 (.10093)	-520.63764 (.75885)
SP1	-534.87952 (.95749)	-1254.88568 (.97016)	-5480.83217 (.91863)	-415.15019 (.22810)	-520.76870 (.87495)
TSs2	-534.71199 (.79666)	-1254.73314 (.82505)	-5480.68325 (.77686)	-415.00540	-520.62444
SP2	-534.90636 (.98139)	-1254.89521 (.97687)	-5480.83891 (.92281)	-415.14872	-520.77215

[a] Calculated at the CCSD//B3LYP/cc-pVTZ and CCSD(T)//B3LYP/cc-pVTZ (in parenthesis) levels.

Table S4: Total energies (in atomic units) of the NCCNO dimers and trimers[a]

Dimers		**Trimers**	
TSdm1	-520.66492	TStr1	-781.10189
DM1	-520.78466	TStr1'	-781.10190
TSdm2	-520.64755	TR1	-781.22349
DM2	-520.74278	TS1tr2,3[b]	-781.10152
TS1[b]	-520.66351	TStr2	-781.07003
fur[b]	-520.74377	TR2	-781.19330
		TStr3	-781.07088
		TR3	-781.19235

[a] Calculated at the CCSD//B3LYP/cc-pVTZ level.
[b] Calculated at the MR-AQCC(2,2)//UB3LYP/cc-pVTZ level.

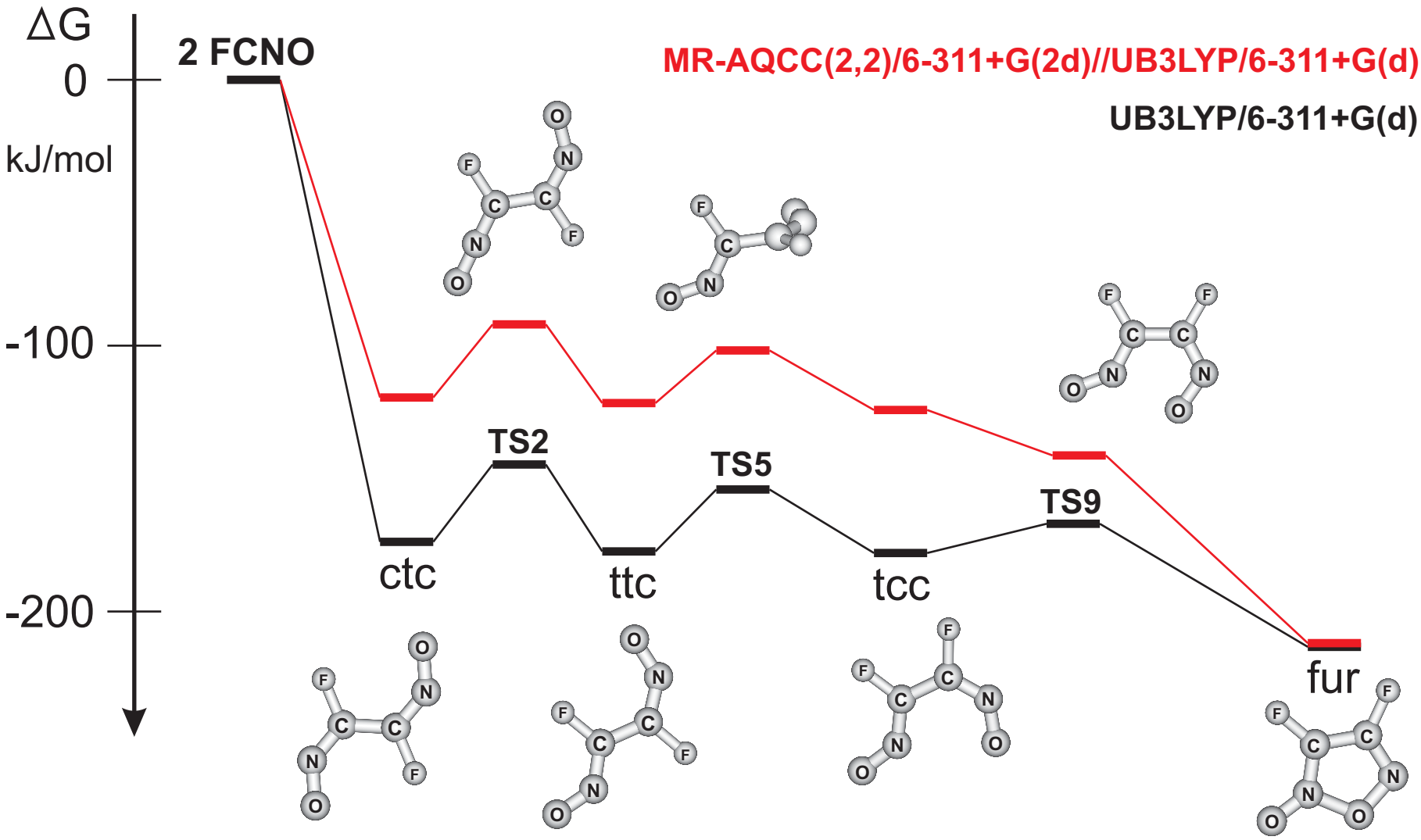


Figure S1

Dimerisation of FCNO

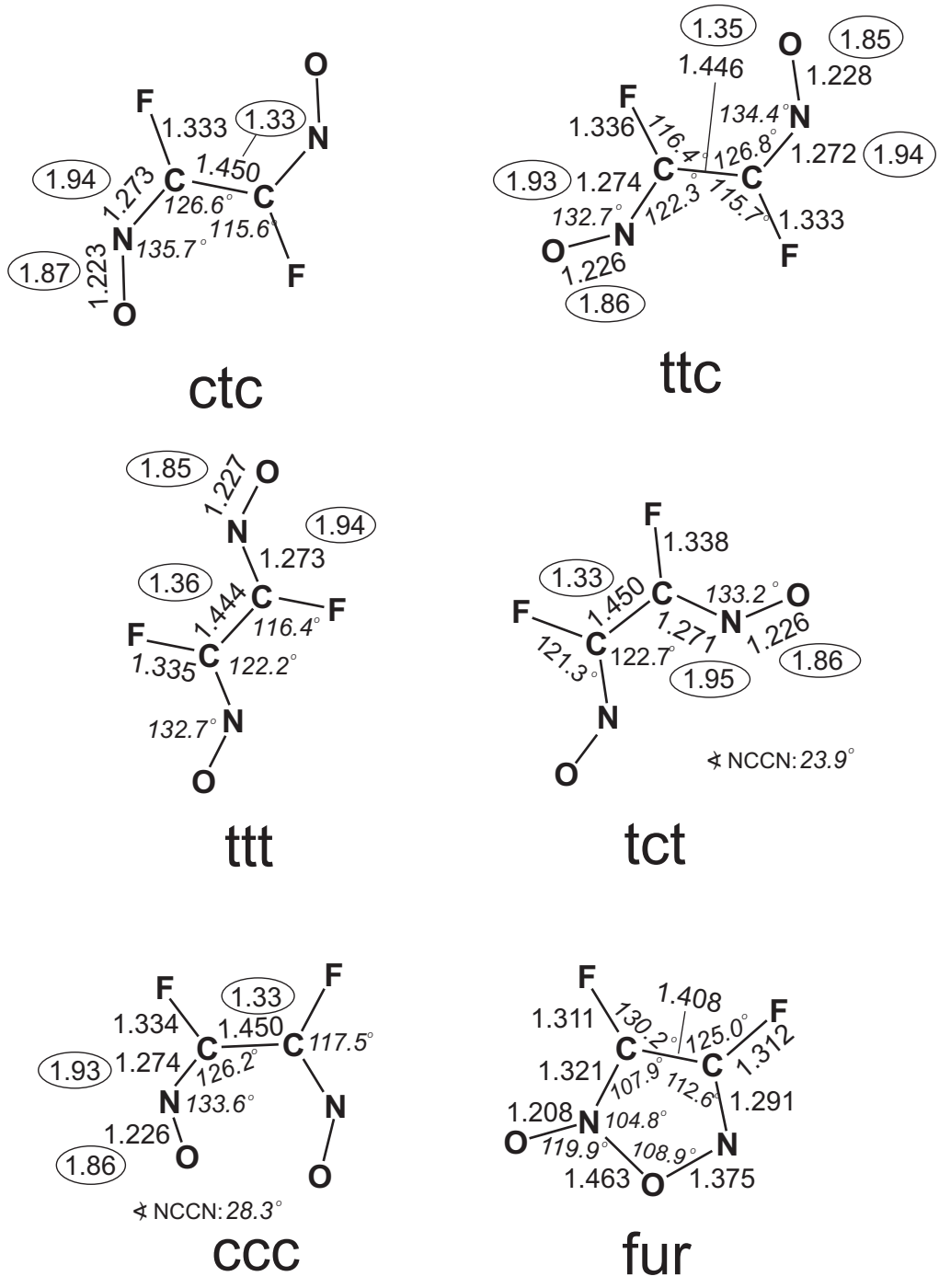


Figure S2

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for FCNO dimerisation (UB3LYP/cc-pVTZ).

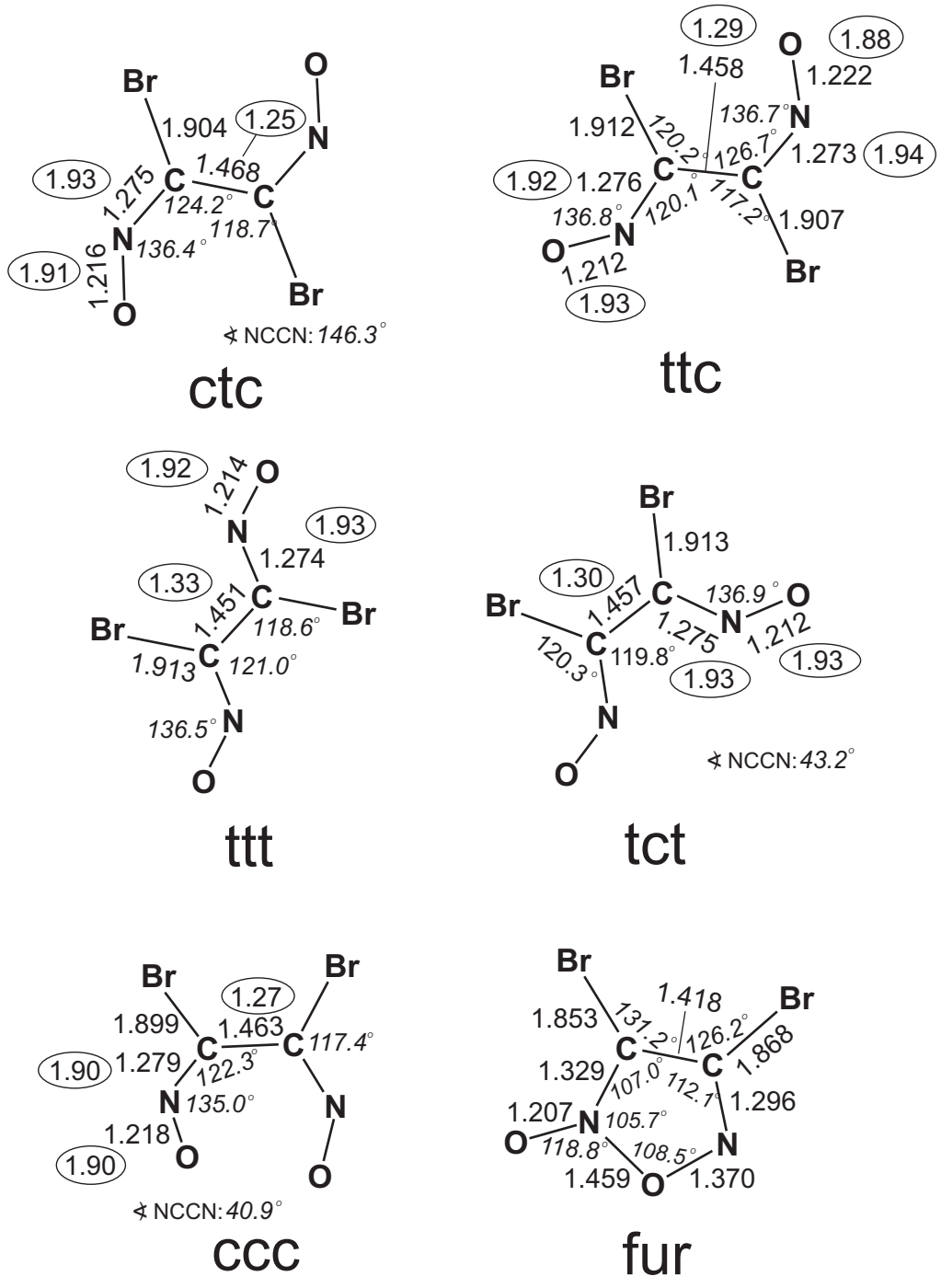


Figure S3

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for BrCNO dimerisation (UB3LYP/cc-pVTZ).

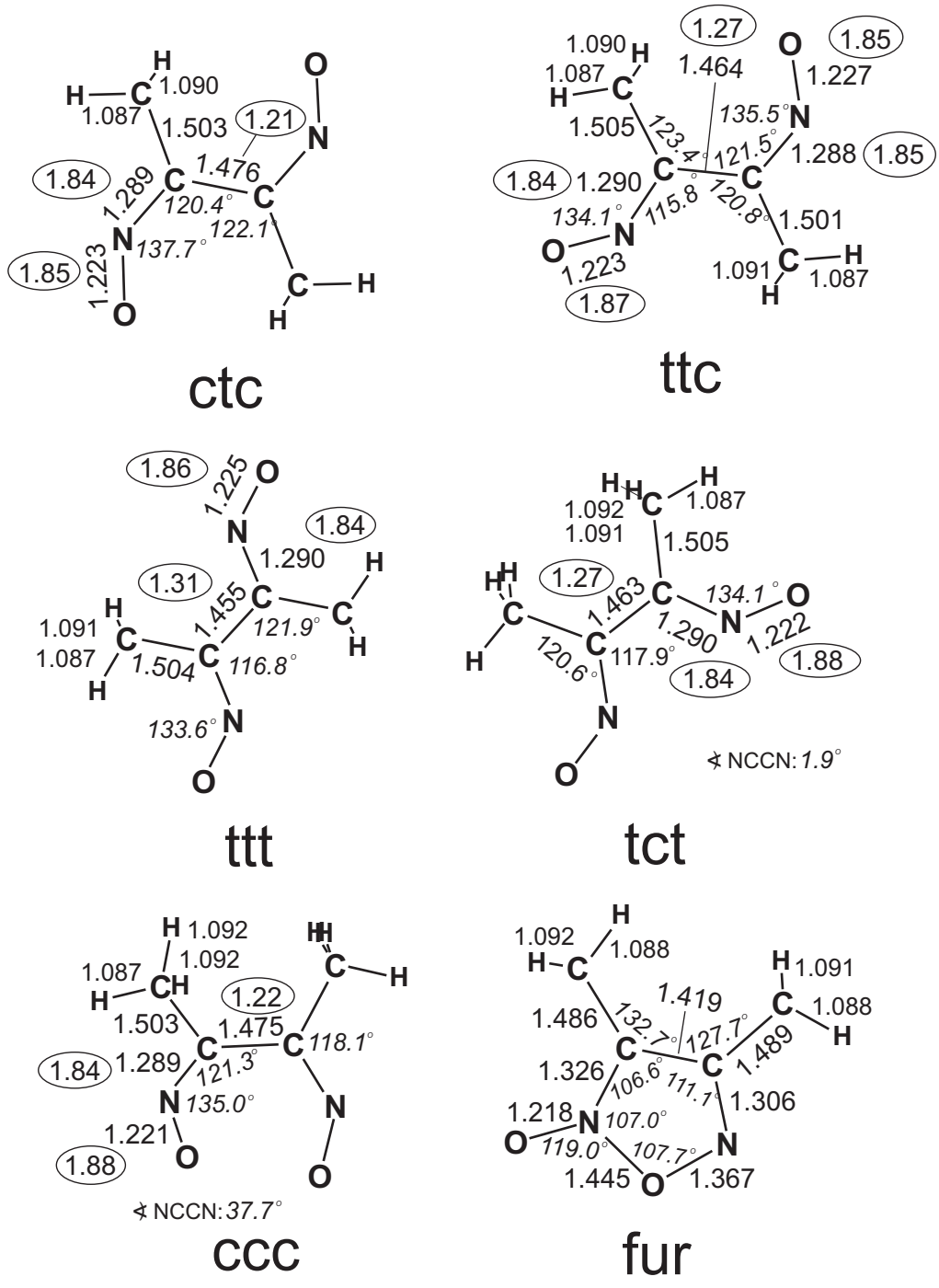


Figure S4

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for CH_3CNO dimerisation (UB3LYP/cc-pVTZ).

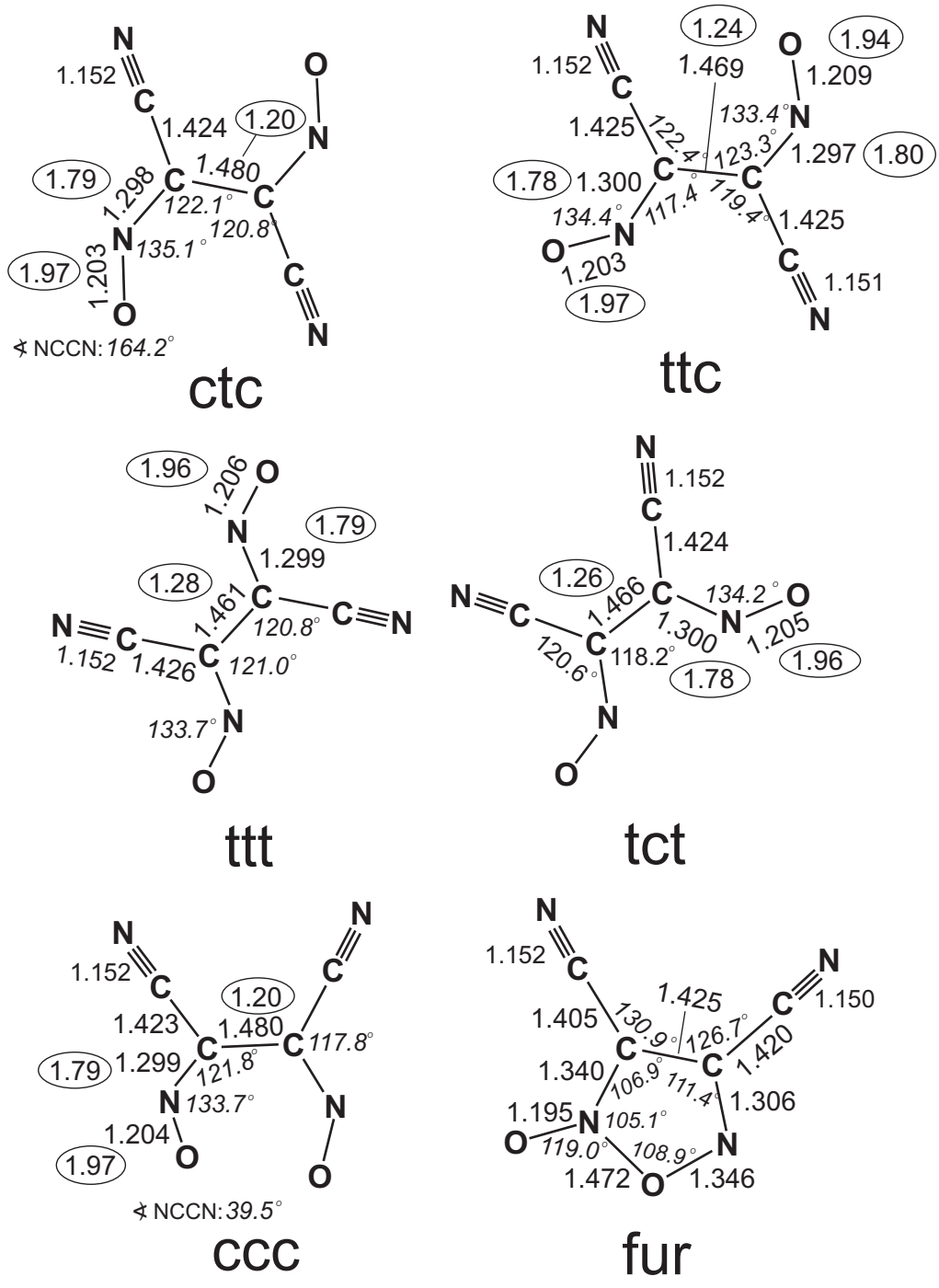


Figure S5

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of minima on the potential energy surface for NCCNO dimerisation (UB3LYP/cc-pVTZ).

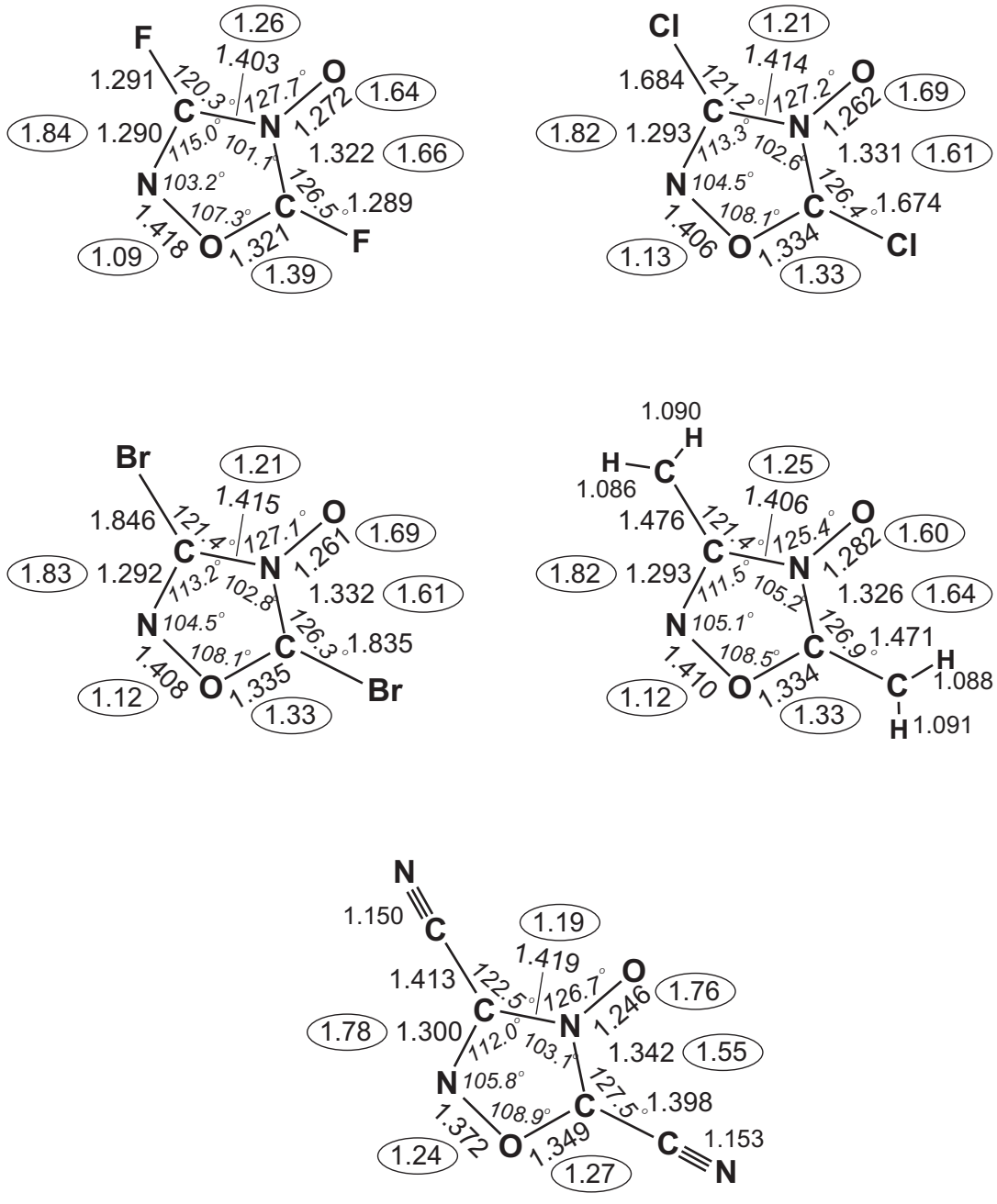


Figure S6

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of 1,2,4-oxadiazole-4-oxides, SP1 (B3LYP/cc-pVTZ).

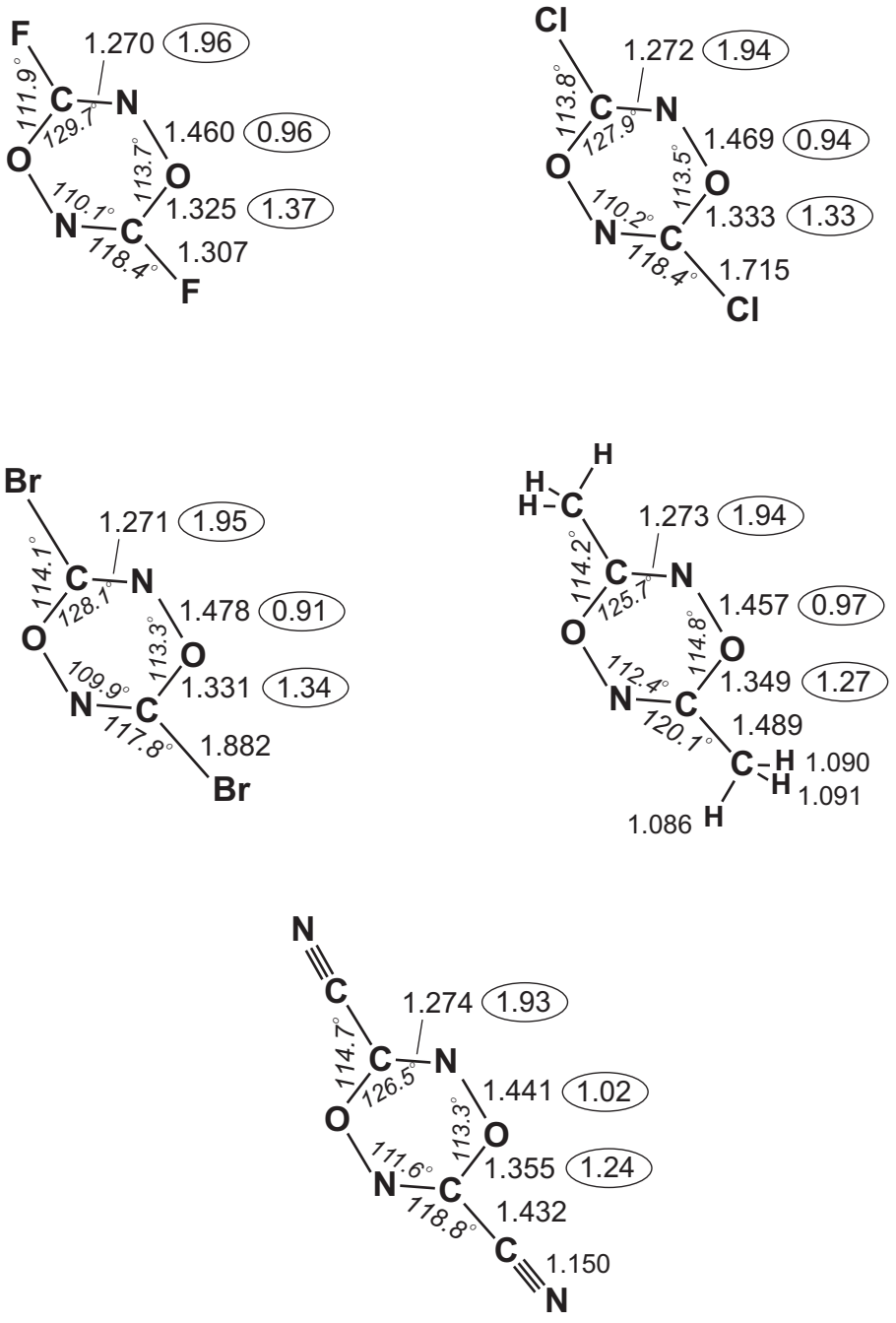
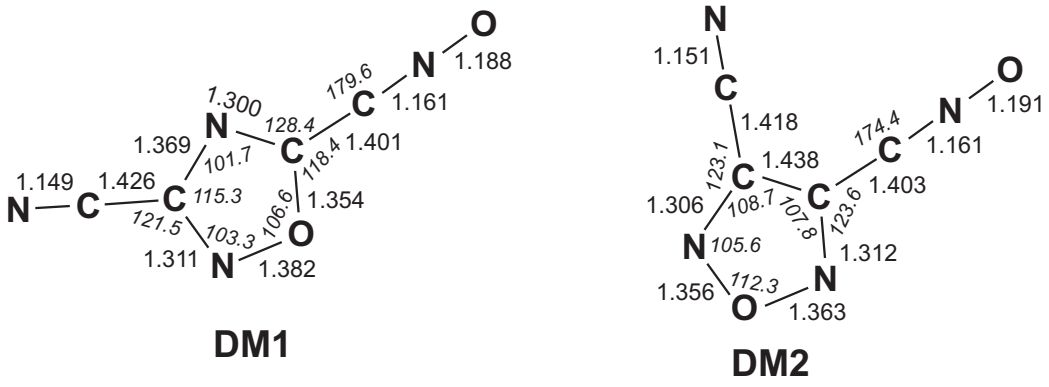
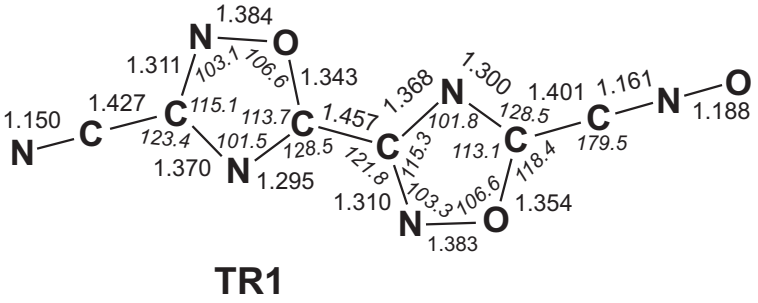


Figure S7

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of 1,4,2,5-dioxadiazines, SP2 (B3LYP/cc-pVTZ).





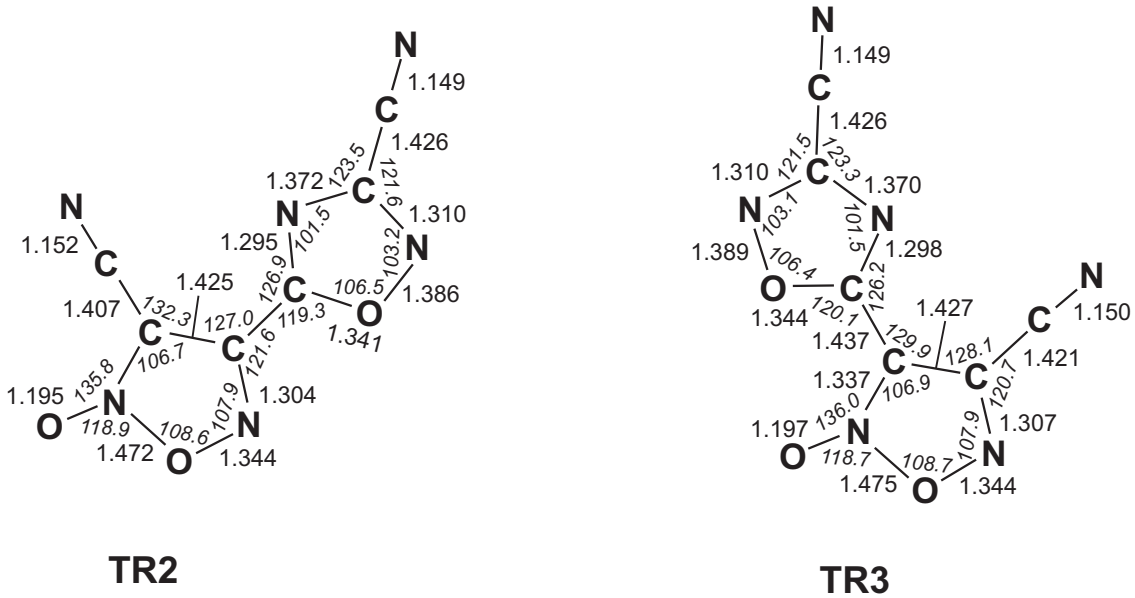


Figure S8

Geometries (bond lengths in Å and bond angles in degrees) and bond orders (circled numbers) of NCCNO dimers and trimers (B3LYP/cc-pVTZ).