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Elucidating the Chemiexcitation of Dioxetanones by Replacing the Peroxide Bond with S-S, N-N and C-C Bonds

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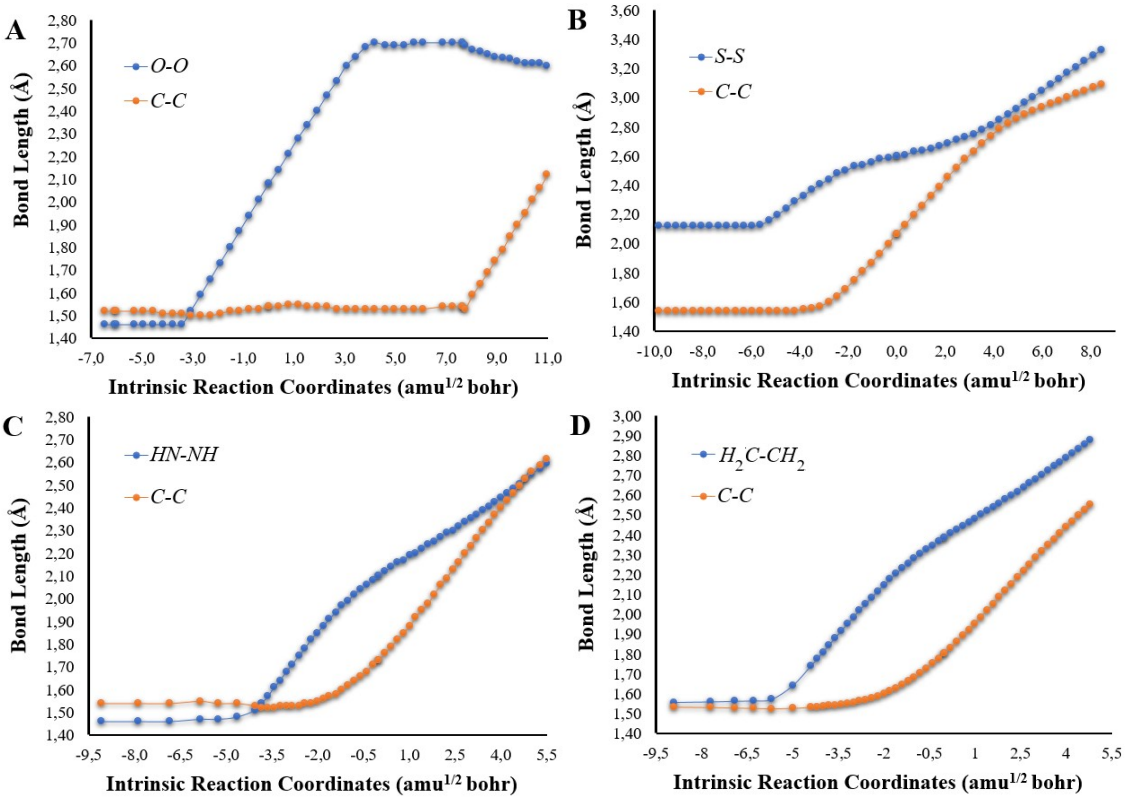


Figure S1 – Bond length (in angström) of the peroxide/non-peroxide and -C-C- bond of the four-membered ring, as a function of intrinsic reaction coordinates, for **Ia** (**A**), **Ib** (**B**), **Ic** (**C**) and **Id** (**D**).

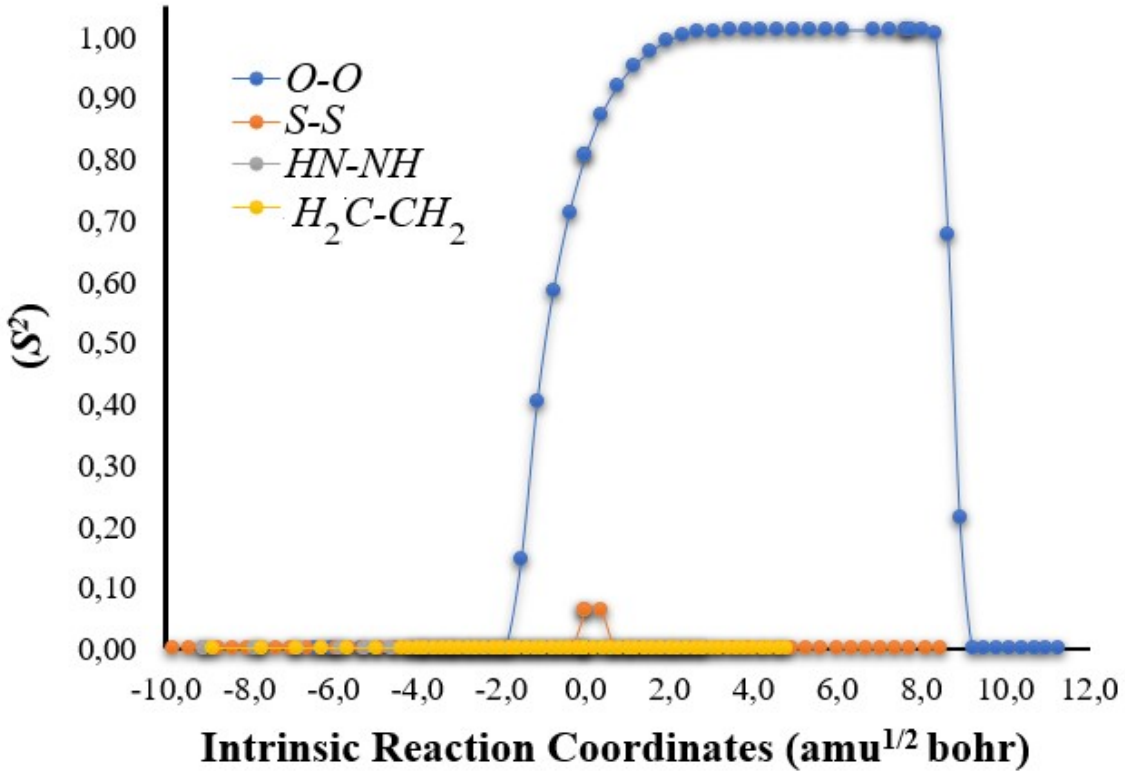
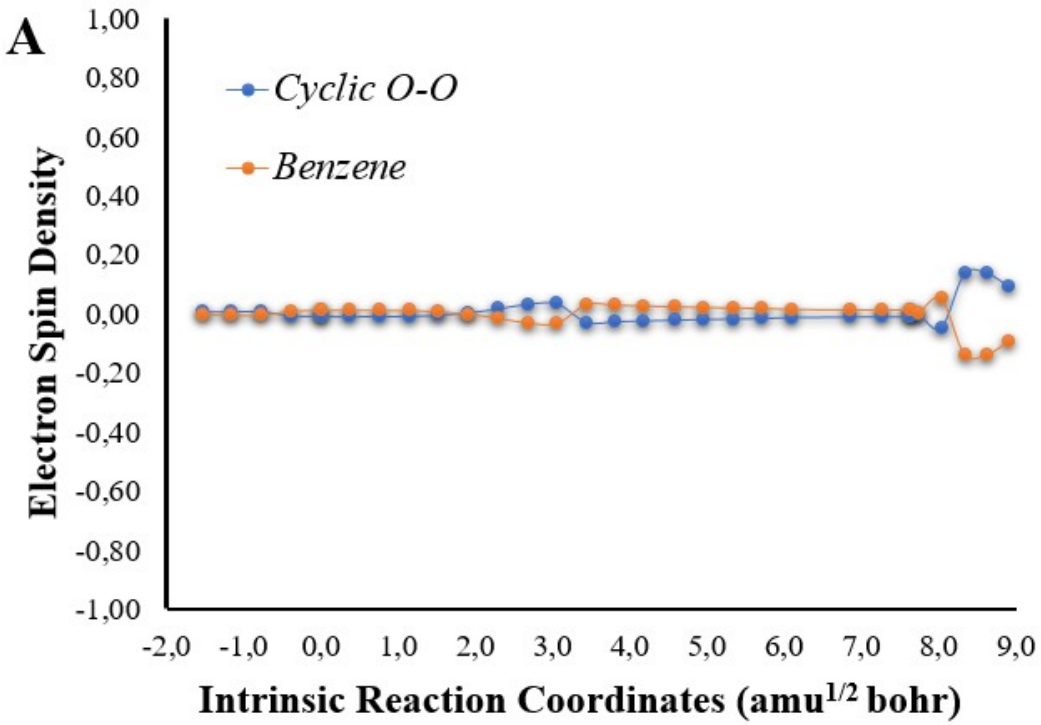


Figure S2 – (S^2) variation as a function of intrinsic reaction coordinates for **Ia-d**.



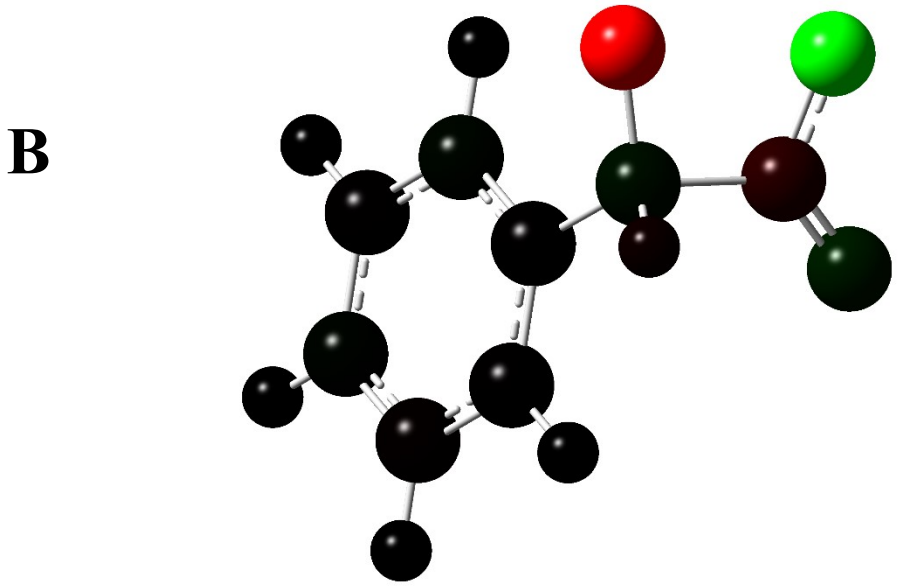


Figure S3 – Electron spin density variation between the cyclic peroxide ring and the benzene moiety of **Ia**, as a function of intrinsic reaction coordinates (**A**). Mulliken spin density of **Ia**, within the biradical region, represented by color atoms by density (**B**).

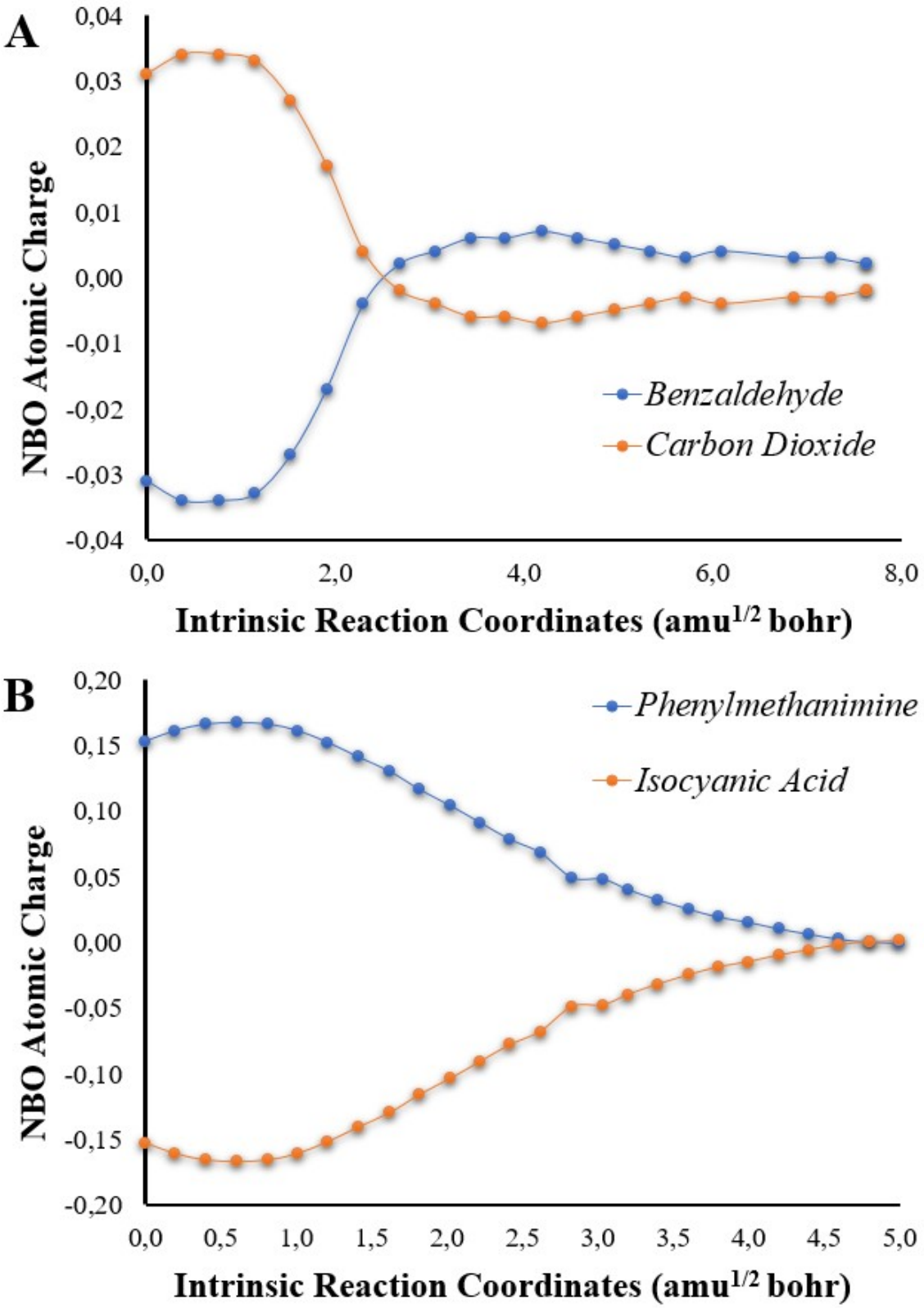


Figure S4 – NBO atomic charge variation, as a function of intrinsic reaction coordinates, between the benzaldehyde and carbon dioxide fragments resulting from the thermolysis of **Ia** (**A**). NBO atomic charge variation, as a function of intrinsic reaction coordinates, between the phenylmethanimine and isocyanic acid fragments resulting from the thermolysis of **Ic** (**B**).

Table S1 – Cartesian coordinates of the transition state for the thermolysis reaction of **Ia**, obtained at the UωB97XD/6-31G(d,p) level of theory.

O	0.73722100	1.61776400	-1.42068200
C	-0.13997500	1.22555900	-0.42806500
C	0.70005200	1.72738800	0.76087800
O	1.75992700	2.32486500	0.24279800
O	0.52958300	1.63578200	1.94294100
C	-0.43599200	-0.25089400	-0.33888400
C	-1.56537000	-0.68029300	0.35585400
C	-1.82264700	-2.04035300	0.48858800
C	-0.95554000	-2.97108700	-0.07707400
C	0.17031200	-2.54024100	-0.77396600
C	0.43511300	-1.18120400	-0.90219700
H	-1.06081600	1.83077600	-0.44396500
H	-2.24132600	0.04746500	0.79636200
H	-2.70158000	-2.37298700	1.03078500
H	-1.15723800	-4.03234800	0.02564400
H	0.84706600	-3.26448700	-1.21544500
H	1.30931700	-0.83362100	-1.44222600

Table S2 – Cartesian coordinates of the transition state for the thermolysis reaction of **Ib**, obtained at the UωB97XD/6-31G(d,p) level of theory.

C	-0.66765300	0.82926300	-0.49421400
C	0.57548600	1.39383000	1.05637900
O	-0.01890400	1.31359400	2.05368100
C	-0.82718300	-0.62862900	-0.30556400
C	-1.93481800	-1.08976300	0.41526700
C	-2.11267600	-2.44834300	0.64542900
C	-1.18084200	-3.36449300	0.16596600
C	-0.06998800	-2.91282500	-0.54307100
C	0.10995300	-1.55570600	-0.77571700
H	-1.51086000	1.43983400	-0.17404700
H	-2.66090100	-0.37602400	0.79484700
H	-2.97950400	-2.79197000	1.20053000
H	-1.31850800	-4.42579900	0.34516400
H	0.66202900	-3.62259300	-0.91477800
H	0.97721700	-1.20446500	-1.32605300
S	0.42765200	1.54848900	-1.53595200
S	2.08951400	1.80994500	0.44915200

Table S3 – Cartesian coordinates of the transition state for the thermolysis reaction of **Ic**, obtained at the UωB97XD/6-31G(d,p) level of theory.

	N	0.23920900	1.87960100	-1.29847200
	C	-0.35574200	1.22678300	-0.25642200
	C	0.95821000	1.84090700	0.68995400
	N	1.98570400	1.70772600	-0.14374800
	O	0.74623500	2.33648700	1.75491200
	C	-0.50080600	-0.26432100	-0.20230000
	C	-1.68654300	-0.80461700	0.29566500
	C	-1.86767600	-2.18307200	0.34310700
	C	-0.86280400	-3.03311200	-0.10713400
	C	0.32626000	-2.49884100	-0.59796000
	C	0.51011600	-1.12210200	-0.64337100
	H	-1.20087400	1.77813100	0.15621700
	H	-2.47376600	-0.14177500	0.64405900
	H	-2.79476200	-2.59220500	0.73128200
	H	-1.00240100	-4.10860000	-0.06987600
	H	1.11828900	-3.15842000	-0.93765700
	H	1.45479200	-0.70871700	-0.98548300
	H	2.80412600	2.20554600	0.22899500
H	0.76124500	1.22406900	-1.88361700	

Table S4 – Cartesian coordinates of the transition state for the thermolysis reaction of **Id**, obtained at the UωB97XD/6-31G(d,p) level of theory.

C	0.67745200	1.88198400	-1.21980300
C	-0.16757600	1.31546200	-0.24576200
C	1.37364800	1.55604100	0.66250500
C	1.58359200	2.92121500	0.73028300
O	2.00388300	0.55960700	0.92638000
C	-0.56574100	-0.11750400	-0.20862400
C	-1.84545600	-0.43459900	0.25289100
C	-2.28182100	-1.75432700	0.29178500
C	-1.43779200	-2.77761400	-0.12648700
C	-0.15721900	-2.47110000	-0.57821600
C	0.27881600	-1.15221300	-0.61896500
H	-0.92693500	1.98629300	0.15050000
H	-2.50931800	0.36031300	0.58221500
H	-3.28041200	-1.98066100	0.65163400
H	-1.77338300	-3.80928800	-0.09535900
H	0.51228600	-3.26425000	-0.89515800
H	1.29015300	-0.93331300	-0.94036300
H	2.45163300	3.29003700	1.27084900
H	0.77407600	3.61406800	0.55114700
H	0.55426100	2.89357700	-1.58045200
H	1.37286400	1.25749100	-1.77143300