

SUPPLEMENTARY MATERIAL for:
Potential-energy surfaces for ring-puckering
motions of flexible cyclic molecules through
Cremer-Pople coordinates: computation, analysis
and fitting

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Contents

1	Suitable choice of the integration grid	
2	Structure associated to each minimum, numeration of each 5-term ring system and 2D-PESs not shown in the main article	
2.1	Cyclopentane	
2.1.1	Numeration	
2.1.2	3D structure	
2.2	1,2-dioxolane	
2.2.1	Numeration	
2.2.2	3D structure	
2.3	1,3-dioxolane	
2.3.1	Numeration	
2.3.2	3D structure	
2.3.3	2D-PES	
2.4	1,2-dithiolane	
2.4.1	Numeration	
2.4.2	3D structure	
2.4.3	2D-PES	
2.5	1,3-dithiolane	
2.5.1	Numeration	
2.5.2	3D structure	
2.5.3	2D-PES	
2.6	1,2-oxathiolane	

	2.6.1	Numeration	
	2.6.2	3D structure	
2.7		1,3-oxathiolane	
	2.7.1	Numeration	
	2.7.2	3D structure	
	2.7.3	2D-PES	
2.8		Tetrahydrofuran	
	2.8.1	Numeration	
	2.8.2	3D structures	
	2.8.3	2D-PES	
2.9		Tetrahydrothiophene	
	2.9.1	Numeration	
	2.9.2	3D structure	
	2.9.3	2D-PES	
2.10		3S-chloro-1,2-dithiolane	
	2.10.1	Numeration	
	2.10.2	3D structures	
2.11		3R,5S-dichloro-1,2-dithiolane	
	2.11.1	Numeration	
	2.11.2	3D structures	
	2.11.3	2D-PES	
2.12		3S,5S-dichloro-1,2-dithiolane	
	2.12.1	Numeration	
	2.12.2	3D structure	

3 Fit of 2D-PES: coefficients and technical details

1 Suitable choice of the integration grid

The choice of a suitable integration grid for numerical integrations is of pivotal importance in DFT calculations. For almost all the cases treated in this work the default value used for DFT calculations in Gaussian 16 (corresponding to the insertion, in the input file, of the option 'Int(Grid=UltraFine)') is adequate, but in the case of the cyclopentane molecule the extremely small energy difference (less than 1 cm^{-1}) between first order saddle points and minima of the global PES suggests the choice of a more accurate grid.

For what concerns the cyclopentane molecule, all the calculations illustrated and discussed in the main article have been carried out with the selection of a specific grid (through the insertion of the option 'Int(Grid=-96040)' in the input file, corresponding to the light blue curve of figure SI 1) of the type 96,40,80 (the grid selected when the option 'Int(Grid=-96032)' is specified is of the type 96,32,64): the first number corresponds to the number of radial shells around each atom, the second and the third numbers define a spherical product grid of dimensions 40,80 in each shell; with this integration grid, the total number of integration points for each atom is $2 \cdot 96 \cdot (40)^2 = 307200$ (the total number of integration points for each atom is $2 \cdot 96 \cdot (32)^4 = 196608$ when the option 'Int(Grid=-96032)' is specified).

In figure SI 1 the one dimensional cut (along the pseudorotation angle θ) of the global PES (1D-PES) of cyclopentane molecule is shown. Results are obtained at B3LYP/6-31G* level of theory. A different choice for the integration grid is the only difference among calculations performed to obtain results displayed in figure SI 1. On the basis of the arguments already discussed in the main article, it is clear that the symmetry displayed by the violet curve (and also, although less evidently, by the red curve) is not correct: there are contribution to the energy which are due to an unsuitable accuracy of the numerical integration.

It should be pointed out that the integration grid used greatly affect the computational cost: the number of integration points for each atom if 'Int(Grid=Superfine)' is specified in the input file is equal to 170450, while the number of integration points for each atom if the default 'pruned' integration grid is used (requested with 'Int(Grid=Ultrafine)') is of 58410. For this reason the default integration grid has been used for all the other molecules studied in this work.

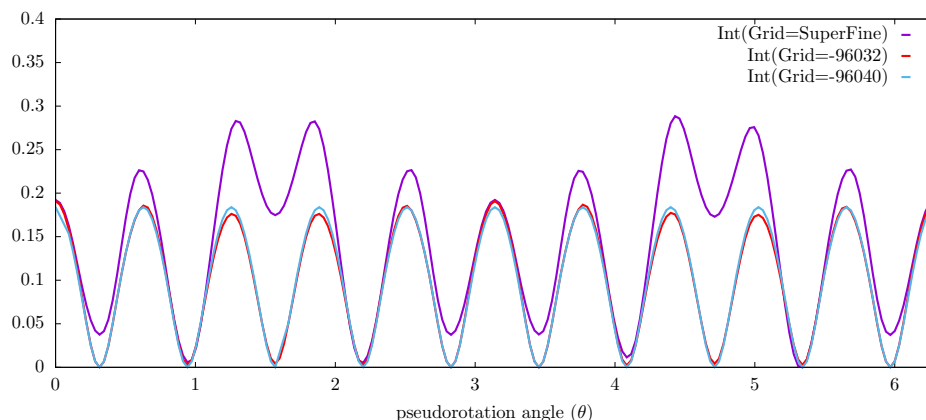


Figure SI 1: 1D-PES of cyclopentane molecule with a constant value of puckering amplitude (0.37) and a value of pseudorotation angle varying in the interval $(0, 2\pi)$; the energies (y axes), relative to the absolute minimum, are in cm^{-1} .

2 Structure associated to each minimum, numeration of each 5-term ring system and 2D-PESs not shown in the main article

In this section the optimized structure of each conformer from different perspectives is reported; each geometry is optimized at the B2PLYPD3/maug-cc-pVTZ level of theory. Each optimization has been performed with the Gaussian 16 suite of programs, specifying the option 'opt=VTight' in the input file. The seven 2D-PESs not shown in the main article are also reported in this section.

In order to employ Cremer-Pople coordinates the vertices of each 5-term ring system must be numbered: specifying the numeration is important in order to reproduce the 2D-PESs displayed both in the main article and in this section; the use of a different numeration for the vertices of the ring system can lead to a phase shift in the pseudorotation angle (remember that, however, adjacent vertexes must be numbered with consecutive integer number). Therefore, in this section the numeration used for each 5-term ring system studied is provided.

When, for the same system, different structures are associated with different energy minima identified on the 2D-PES, each structure is labeled with consecutive roman numbers in ascending order of energy. Due to the inherent chirality of the 5-term rings studied, sometimes different (enantiomeric) structures are associated with the same energy value (although with different Cremer-Pople coordinates and so with different points of the corresponding 2D-PES): for these cases, in this section the image of only one enantiomer is displayed (the structure of the other enantiomer can be straightforwardly obtained by taking the mirror image of the displayed structure).

2.1 Cyclopentane

2.1.1 Numeration

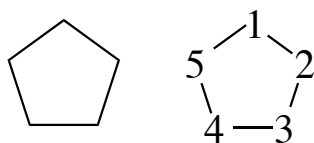


Figure SI 2: Numeration employed for the use of Cremer-Pople coordinates

2.1.2 3D structure

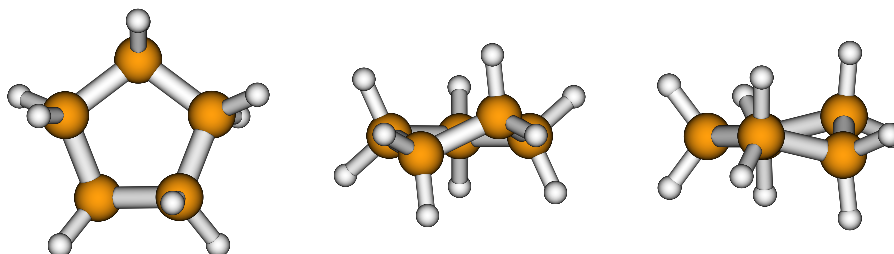


Figure SI 3: Optimized structure of cyclopentane from three different perspectives

2.2 1,2-dioxolane

2.2.1 Numeration

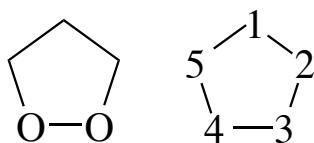


Figure SI 4: Numeration employed for the use of Cremer-Pople coordinates

2.2.2 3D structure

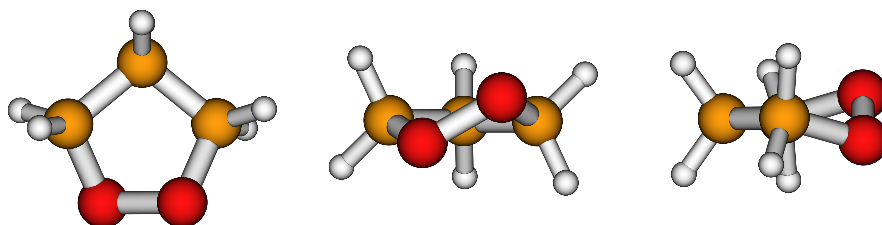


Figure SI 5: Optimized structure of 1,2-dioxolane from three different perspectives

2.3 1,3-dioxolane

2.3.1 Numeration

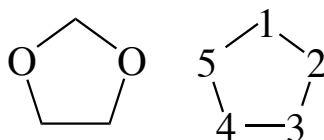


Figure SI 6: Numeration employed for the use of Cremer-Pople coordinates

2.3.2 3D structure

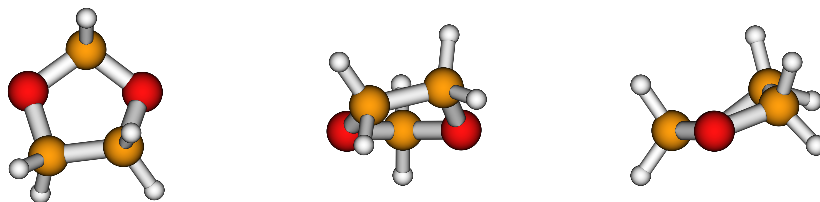


Figure SI 7: Optimized structure of 1,3-dioxolane from three different perspectives

2.3.3 2D-PES

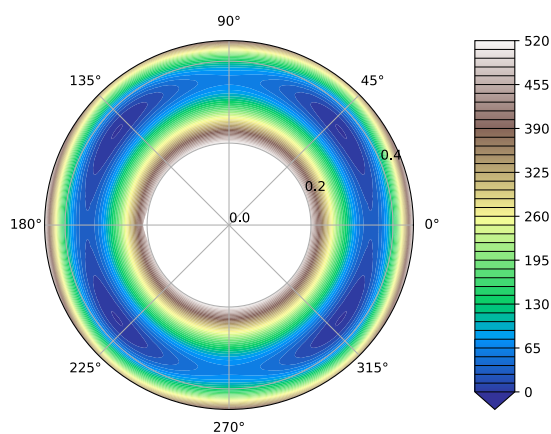


Figure SI 8: 2D-PES of 1,3-dioxolane; energy values (given on the right of the colorbar) are in cm^{-1} ; the figure is shown only in the interval $0.2 < q < 0.45$ in order to account for the slightly hindered pseudorotational motion of 1,3-dioxolane molecule.

2.4 1,2-dithiolane

2.4.1 Numeration

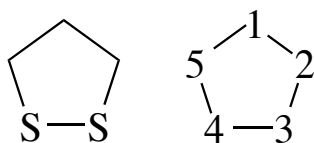


Figure SI 9: Numeration employed for the use of Cremer-Pople coordinates

2.4.2 3D structure

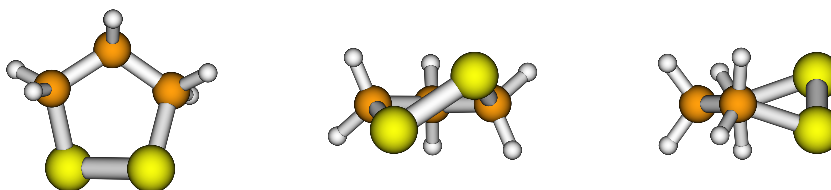


Figure SI 10: Optimized structure of 1,2-dithiolane from three different perspectives

2.4.3 2D-PES

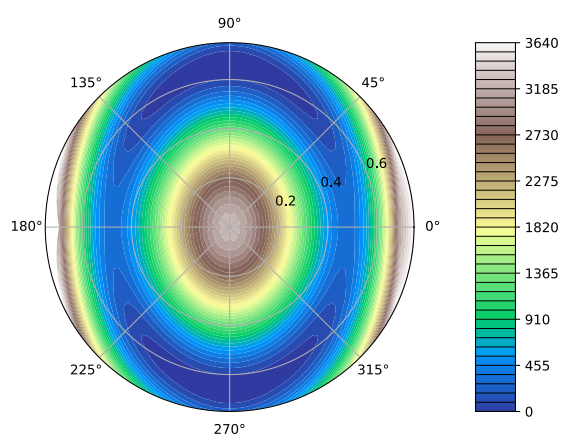


Figure SI 11: 2D-PES of 1,2-dithiolane; energy values (given on the right of the colorbar) are in cm^{-1} .

2.5 1,3-dithiolane

2.5.1 Numeration

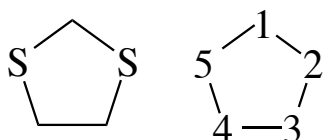


Figure SI 12: Numeration employed for the use of Cremer-Pople coordinates

2.5.2 3D structure

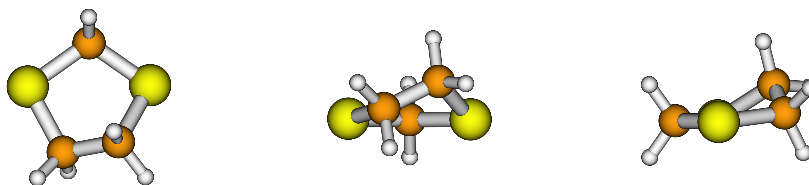


Figure SI 13: Optimized structure of 1,3-dithiolane from three different perspectives

2.5.3 2D-PES

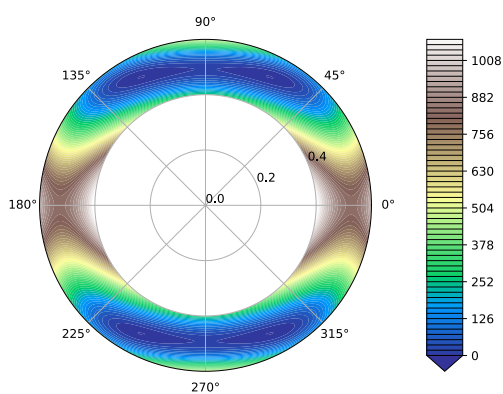


Figure SI 14: 2D-PES of 1,3-dithiolane; energy values (given on the right of the colorbar) are in cm^{-1} ; computational results are displayed in the interval $0.4 < q < 0.6$ to the purpose of highlighting the change of energy values along the pseudorotational circuit

2.6 1,2-oxathiolane

2.6.1 Numeration

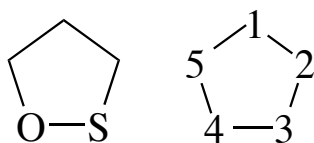


Figure SI 15: Numeration employed for the use of Cremer-Pople coordinates

2.6.2 3D structure

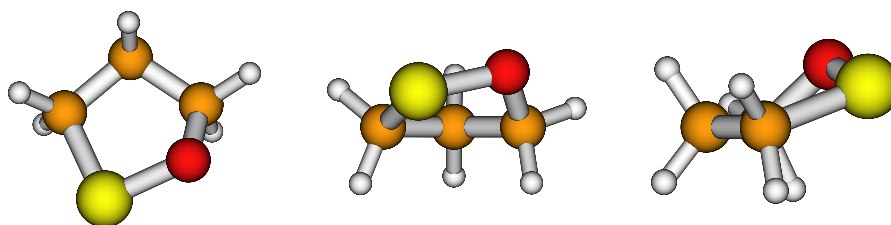


Figure SI 16: Optimized structure of 1,2-oxathiolane from three different perspectives

2.7 1,3-oxathiolane

2.7.1 Numeration

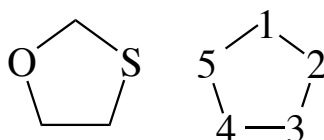


Figure SI 17: Numeration employed for the use of Cremer-Pople coordinates

2.7.2 3D structure

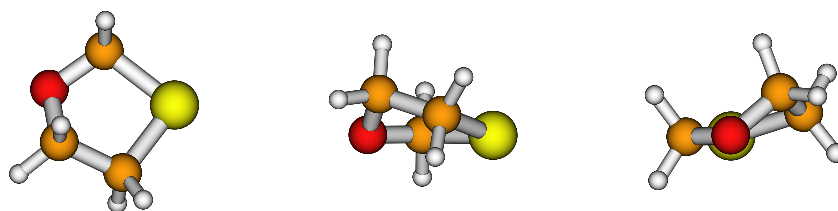


Figure SI 18: Optimized structure of 1,3-oxathiolane from three different perspectives

2.7.3 2D-PES

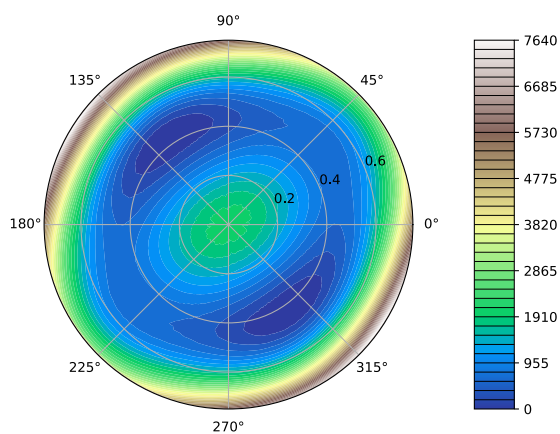


Figure SI 19: 2D-PES of 1,3-oxathiolane; energy values (given on the right of the colorbar) are in cm^{-1} .

2.8 Tetrahydrofuran

2.8.1 Numeration

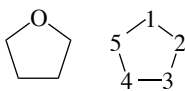


Figure SI 20: Numeration employed for the use of Cremer-Pople coordinates

2.8.2 3D structures

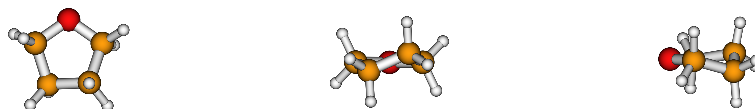


Figure SI 21: Optimized structure of conformer I of tetrahydrofuran from three different perspectives

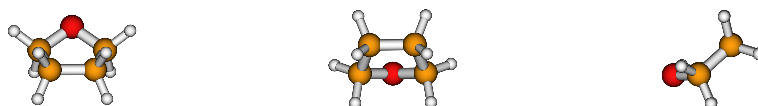


Figure SI 22: Optimized structure of conformer II of tetrahydrofuran from three different perspectives

2.8.3 2D-PES

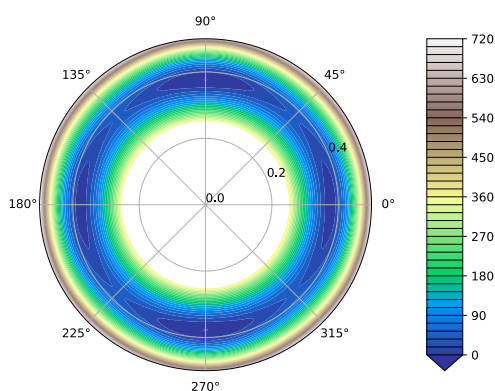


Figure SI 23: 2D-PES of tetrahydrofuran; energy values (given on the right of the color-bar) are in cm^{-1} ; computational results are displayed only in the interval $0.25 < q < 0.5$ with the aim of highlighting the main features of the pseudorotational path.

2.9 Tetrahydrothiophene

2.9.1 Numeration

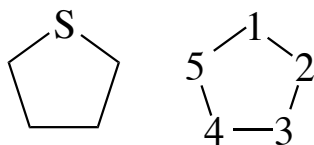


Figure SI 24: Numeration employed for the use of Cremer-Pople coordinates

2.9.2 3D structure

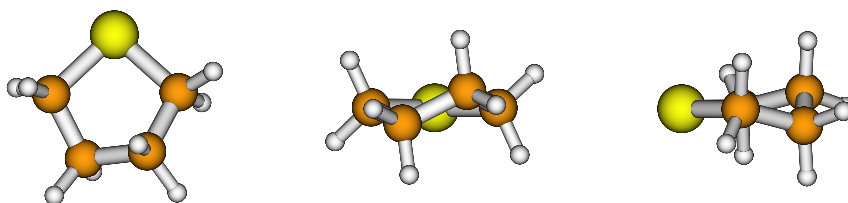


Figure SI 25: Optimized structure of tetrahydrothiophene from three different perspectives

2.9.3 2D-PES

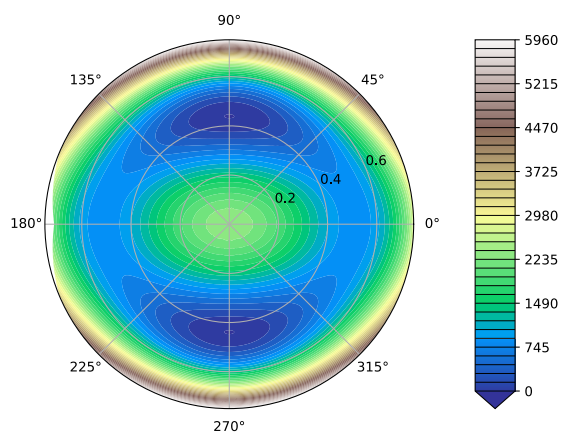


Figure SI 26: 2D-PES of tetrahydrothiophene; energy values (given on the right of the colorbar) are in cm^{-1} .

2.10 3S-chloro-1,2-dithiolane

2.10.1 Numeration

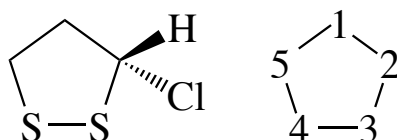


Figure SI 27: Numeration employed for the use of Cremer-Pople coordinates

2.10.2 3D structures

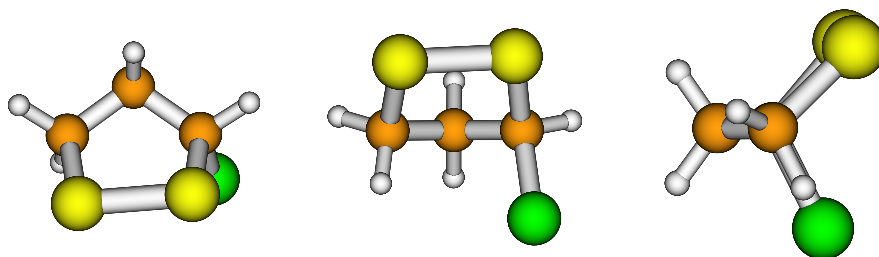


Figure SI 28: Optimized structure of conformer I of 3S-chloro-1,2-dithiolane from three different perspectives

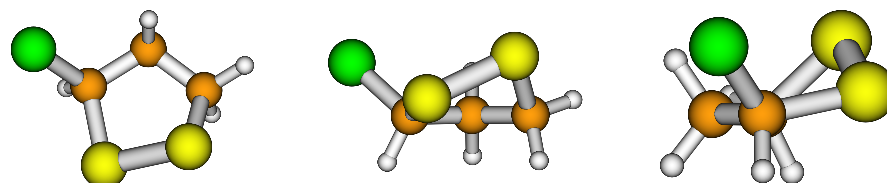


Figure SI 29: Optimized structure of conformer II of 3S-chloro-1,2-dithiolane from three different perspectives

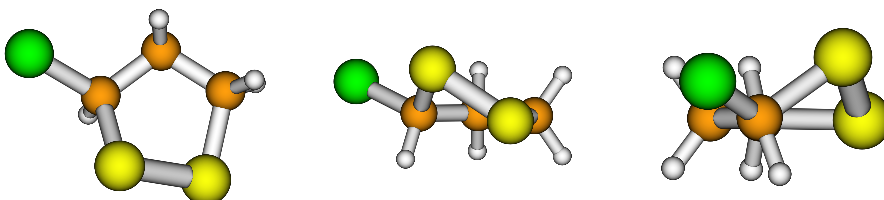


Figure SI 30: Optimized structure of conformer III of 3S-chloro-1,2-dithiolane from three different perspectives

2.11 3R,5S-dichloro-1,2-dithiolane

2.11.1 Numeration

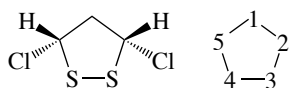


Figure SI 31: Numeration employed for the use of Cremer-Pople coordinates

2.11.2 3D structures

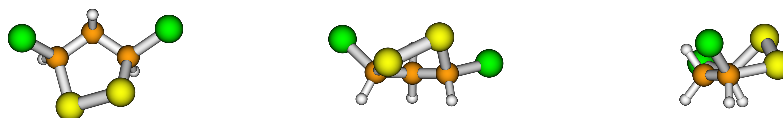


Figure SI 32: Optimized structure of conformer I of 3R,5S-dichloro-1,2-dithiolane from three different perspectives

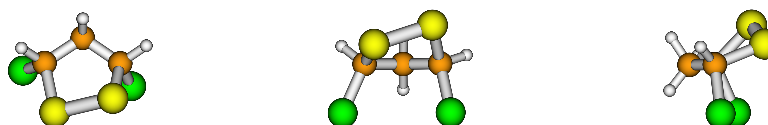


Figure SI 33: Optimized structure of conformer II of 3R,5S-dichloro-1,2-dithiolane from three different perspectives

2.11.3 2D-PES

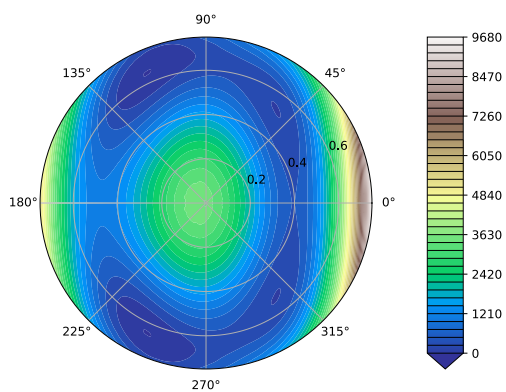


Figure SI 34: 2D-PES of 3R,5S-dichloro-1,2-dithiolane; energy values (given on the right of the colorbar) are in cm⁻¹.

2.12 3S,5S-dichloro-1,2-dithiolane

2.12.1 Numeration

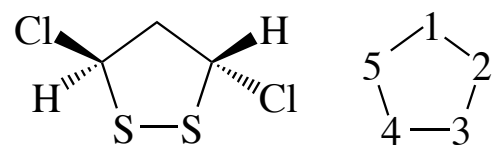


Figure SI 35: Numeration employed for the use of Cremer-Pople coordinates

2.12.2 3D structure

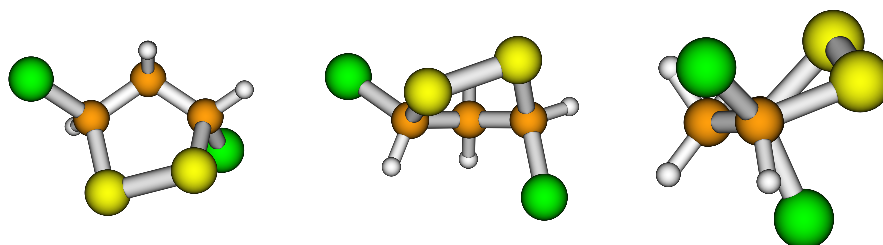


Figure SI 36: Optimized structure of 3S,5S-dichloro-1,2-dithiolane from three different perspectives

3 Fit of 2D-PES: coefficients and technical details

In this section some remarks and technical details on the fit of the 2D-PESs are provided. The coefficients obtained through linear fit are given in table SI 1 (the definition of each term can be easily found in the main article). When the energy difference between the first order saddle points and the minima encountered along the pseudorotational path is very small, in order to obtain a good fit of the pseudorotational path a certain number of points used to sample the 2D-PES has been discarded when the fit was carried out: essentially, each point is retained or discarded on the basis of its inclusion or exclusion from an interval $q_{min} < x < q_{max}$, where x is the puckering amplitude associated to that point and q_{min} and q_{max} have been chosen with the aim of performing the fit with all the points pertaining to or adjacent to the pseudorotational path. An alternative solution to this problem (not explored in this work) would be a fit carried out with the inclusion of all the points used for the sampling of the 2D-PES with different weights (for example, a weight inversely proportional to the energy associated to a specific point). However, for what concerns the systems studied in this work the approximated solution chosen should be fairly accurate.

The known argument a has a transparent physical meaning: it corresponds to the energy associated to the barrier to planarity and, therefore, its value has been automatically set equal to the energy associated to the planar conformation of the 5-term ring ($q = 0$, corresponding to a second order saddle point of the global PES for 9 of the 12 systems studied in this work and close to the second order saddle point of the global PES for the other 3 systems) instead of determining its value through the linear fit.

In the list below the values of q_{min} and q_{max} and the number of points used to carry out the linear fit ¹ (in parenthesis the total number of points available) are reported for 4 of the 12 systems studied. For all the other cases, the linear fit has been performed employing all the available points.

- cyclopentane: $q_{min} = 0.38$, $q_{max} = 0.44$, number of points used: 1131 (9431);
- tetrahydrofuran: $q_{min} = 0.2$, $q_{max} = 0.5$, number of points used: 2953 (5017);
- 1,3-dioxolane: $q_{min} = 0.2$, $q_{max} = 0.5$, number of points used: 2953 (7845);
- 1,3-dithiolane: $q_{min} = 0.2$, $q_{max} = 0.7$, number of points used: 4017 (5025).

¹it should be underlined that "the number of points used to carry out the linear fit" is different from the number of calculated point reported in table II (see the main article): the reason is the possibility of exploit the symmetry to reduce the number of points which are to be calculated in order to sample uniformly the interval $[0, 2\pi]$ of θ values. The only case in which the number of calculated points coincide with the number of points used to carry out the linear fit is the 3-chloro-1,2-dithiolane molecule (because in this case the molecule belongs to the C_1 symmetry point group and the symmetry cannot be exploited to reduce the number of calculations needed).

The high number of points used to perform the linear fit raise an issue concerning the minimum number of points needed to carry out an accurate linear fit. To address this issue, the results of a series of fits which give a coefficient of determination close to 1 ($R^2 \simeq 1$) using the same functional form reported in the main article with a smaller number of points for most of the molecules considered in this work is given in table SI 2. Although the coefficients are not reported, the adequacy of the results obtained for each linear fit are checked by visual inspection through a comparison with 2D-PES reported in the main article. The results reported in table SI 2 clearly suggest that a smaller number of points than the one used in this work is sufficient to obtain an accurate analytical representation of the 2D-PES. When the increment of the sampling interval affects relevantly the result of the fit the corresponding entry of table SI 2 is left blank. For example, the increment of the sampling interval to a value of 4Δ for 3S-chloro-1,2-dithiolane leads to an analytical form for the corresponding 2D-PES which differs even qualitatively (with the appearance of a fourth minimum that is absent when more points are used for the linear fit) from the 2D-PES reported in figure 12 (see the main article). Cyclopentane is not

molecule	coefficients																				R^2
	a (fixed)	b_{-1}^c	b_{-1}^s	b_{-1}^i	b_{-2}^c	b_{-2}^s	b_{-2}^i	b_{-3}^c	b_{-3}^s	b_{-3}^i	b_{-4}^c	b_{-4}^s	b_{-4}^i	b_{-5}^c	b_{-5}^s	b_{-5}^i	b_{-10}^c	b_{-10}^s	b_{-10}^i		
cyclopentane	1768	-20908	61763	0	0	0	0	0	0	0	0	0	0	0	0	0	0	28	-154	0.9994	
tetrahydrofuran	1218	-16850	58952	0	0	0	-14	366	0	0	0	0	-126	174	0	0	0	0	0	0.997	
tetrahydrothiophene	2341	-16457	37064	0	0	0	4953	-14558	0	0	0	0	-16	-947	0	0	0	0	0	0.994	
1,2-dioxolane	2380	-19116	50596	0	0	0	1524	2553	0	0	0	0	0	0	0	0	0	0	0	0.994	
1,3-dioxolane	1049	-16239	64278	0	0	0	-765	5156	0	0	0	0	93	632	0	0	0	0	0	0.999	
1,2-dithiolane	3243	-19904	32934	0	0	0	-4283	15460	0	0	0	0	388	337	0	0	0	0	0	0.994	
1,3-dithiolane	2280	-14366	25503	0	0	0	3880	-8888	0	0	0	0	159	1683	0	0	0	0	0	0.998	
1,2-oxathiolane	2301	-17858	40994	0	0	0	-972	7767	3044	-8885	0	0	-15	373	-106	1423	0	0	0	0.995	
1,3-oxathiolane	2032	-15925	39974	0	0	0	1062	-2424	4291	-15225	0	0	211	74	232	-1781	0	0	0	0.997	
3R,5S-dichloro-1,2-dithiolane	3488	-20417	36621	-3464	12496	0	-4386	19752	0	-78	1395	0	978	763	0	0	0	0	0	0.981	
3S,5S-dichloro-1,2-dithiolane	3515	-20899	35479	0	0	-4160	8855	-5631	18554	0	0	142	417	467	929	0	0	0	0	0.984	
3-chloro-1,2-dithiolane	3584	-20082	32904	-2892	5498	-1715	3538	-4668	15927	0	-458	585	0	500	547	0	-28	329	0	0.982	

Table SI 1: Coefficients obtained for each molecule through linear fit

molecule	Δ		2Δ		3Δ		4Δ		5Δ		6Δ		7Δ	
	number of points	R^2	number of points	R^2	number of points	R^2	number of points	R^2	number of points	R^2	number of points	R^2	number of points	R^2
tetrahydrofuran	2953	0.997	741	0.997	325	0.997	185	0.997	117	0.998	85	0.998	61	0.9988
tetrahydrothiophene	5025	0.994	1257	0.994	553	0.994	317	0.994	197	0.994	137	0.995	101	0.995
1,2-dioxolane	5025	0.994	1257	0.994	553	0.993	317	0.994	197	0.993	137	0.995	101	0.995
1,3-dioxolane	2953	0.999	741	0.999	325	0.999	185	0.999	117	0.999	85	0.999	61	0.999
1,2-dithiolane	5025	0.994	1257	0.994	553	0.995	317	0.994	197	0.994	137	0.995	101	0.995
1,3-dithiolane	4017	0.998	1005	0.998	453	0.998	257	0.998	165	0.998	113	0.998	81	0.998
1,2-oxathiolane	2629	0.995	665	0.995	293	0.995	169	0.995	101	0.995	69	0.996	57	0.997
1,3-oxathiolane	2453	0.997	613	0.997	277	0.997	149	0.997	97	0.997	69	0.997	49	0.998
3R,5S-dichloro-1,2-dithiolane	1257	0.981	317	0.980	137	0.983	81	0.979	49	0.985	37	0.992	-	-
3S,5S-dichloro-1,2-dithiolane	1257	0.984	317	0.983	137	0.985	81	0.982	-	-	-	-	-	-
3S-chloro-1,2-dithiolane	1257	0.982	317	0.981	137	0.983	-	-	-	-	-	-	-	-

Table SI 2: Stability of the linear fit as a function of the sampling interval (Δ) and the total number of points used; the value of Δ is given in the main article (see table II), as the functional form used for each molecule (see table III).