Electronic Supplementary Information (ESI)

Potential energy surfaces of a stacked dimer of benzene and its radical cation: what remains and what appears

Irina V. Beregovaya,* Lyudmila N. Shchegoleva

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, 9 Ac. Lavrentiev Avenue, Novosibirsk 630090, Russia; E-mail: ivb@nioch.nsc.ru

1. Parallel-displaced structures of the neutral benzene dimer and its radical cation. The magnitudes of the shift

2. Table S1. Total (E, a.u.) and relative (ΔE, kcal/mol) energies of the stationary stractures of $(C_6H_6)_2^{+\cdot}$

3. Degenerate transformations of the orbital isomeric structures of the benzene dimer radical cation. The data of DFT calculations

4. Comparison of potential energy profiles obtained in the B3LYP-D3/6-31G* and EOM-IP-CCSD/cc-pVDZ//B3LYP-D3/6-31G* approximations for the transformations of the stationary structures of $(C_6H_6)_2$

5. Table S2. The averaged hfc constant with protons, $\bar{a}$ (12H), for the minimum energy structures of two orbital isomer of $(C_6H_6)_2^{+\cdot}$. Calculation using the B3LYP-D3/cc-pVDZ method

6. References

7. Cartesian coordinates for structures first described in this work, **F**, **G**, **TS** (GAMESS, B3LYP-D3/6-31G*, angs)

8. Cartesian coordinates for stationary structures of $(C_6H_6)_2^{+\cdot}$ (Orca, EOM-IP-CCSD/cc-pVDZ, angs)

1. Parallel-displaced structures of the neutral benzene dimer and its radical cation. The magnitude of the shift
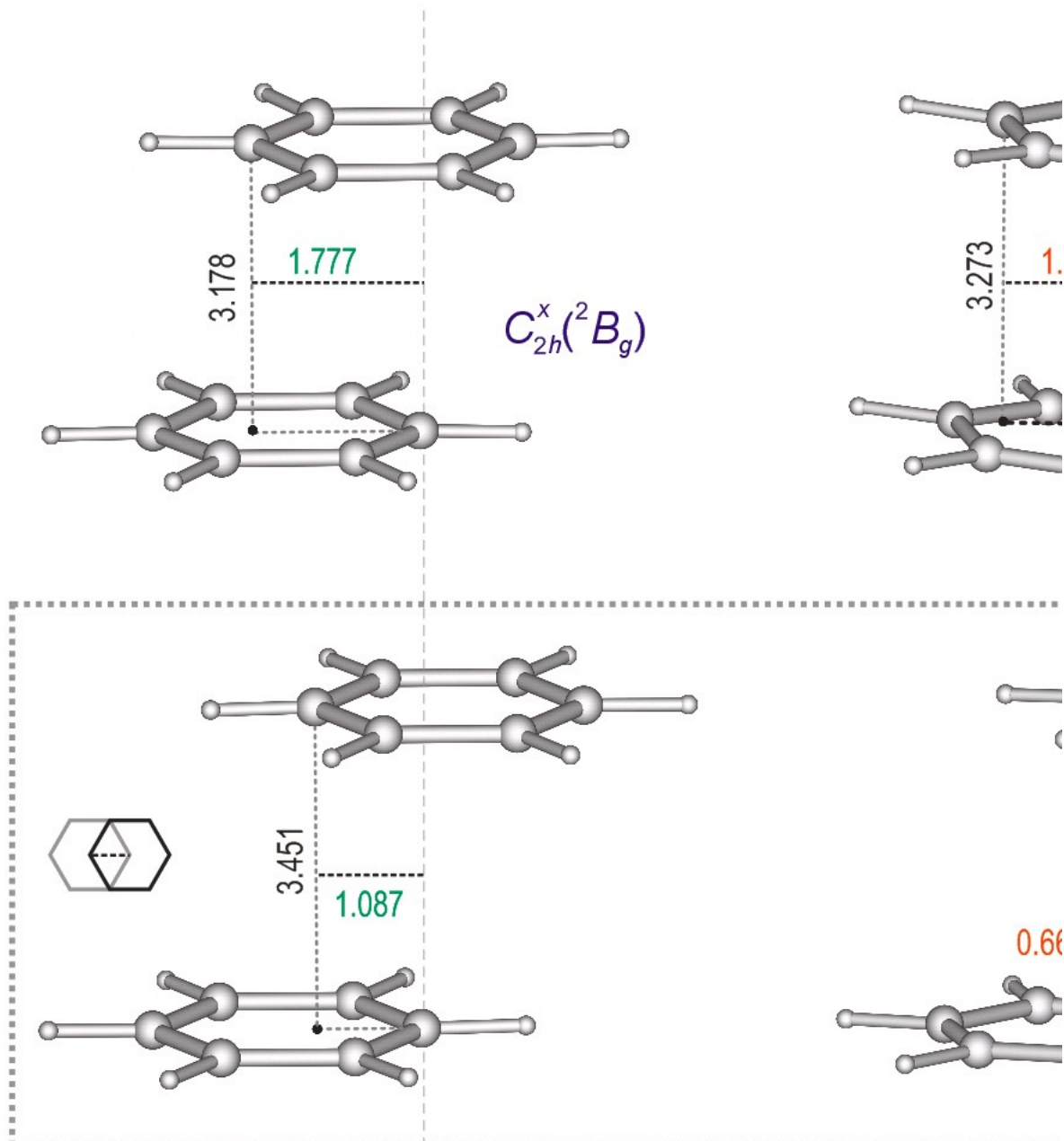

Figure S1. Distances between fragments and relative shifts of the fragments in some stationary structures of the benzene stacked dimer and its radical cation.
Center frame: C_{2h}^x (left) and C_{2h}^y structures of $(C_6H_6)_2$. Above and below are the corresponding structures of the radical cation. The values are given in angstroms. Results of B3LYP-D3/6-31G* calculations.

2. Table S1. Total (E, a.u.) and relative (ΔE, kcal/mol) energies of the stationary structures of $(C_6H_6)_2^{+\cdot}$. [a]

Structure, symmetry	ωB97X-D/cc-pVDZ		ωB97X-D/6-31G*		B3LYP-D3/6-31G*		OO-RI-MP2/cc-pVDZ		EOM-IP-CCSD/cc-pVDZ	
	E (n [b])	ΔE	E (n [b])	ΔE	E (n [b])	ΔE	E	ΔE	E	ΔE
domain **1**										
D $C_{2h}{}^y$ (^2B_g)	-464.06323 (1)	0.11	-464.03753 (1)	0.11	-463.91999 (1)	0.23	-462.769298	0.29	-462.792829	0.15
A $C_{2h}{}^x$ (^2B_g)	-464.06333 (1)	0.05	-464.03766 (1)	0.03	-463.92016 (1)	0.12	**-462.769762**	**0**	**-462.793065**	**0.**
a $C_2{}^x$ (^2B)	**-464.06341 (0)**	**0.**	**-464.03771 (0)**	**0.**	**-463.92035 (0)**	**0.**	- [c]		- [c]	-
F $C_s{}^{yz}$ ($^2A''$)	-464.06327 (1)	0.09	-464.03760 (1)	0.07	-463.92009 (1)	0.16	-462.769442	0.20	-462.792870	0.12
domain **2**										
C $C_{2h}{}^x$ (^2B_u)	-464.05937 (1)	2.54	-464.03437 (1)	2.10	-463.91807 (1)	1.43	**-462.764413**	**3.36**	-462.789738	**2.08**
c $C_2{}^x$ (^2B)	**-464.05942 (0)**	**2.51**	**-464.03440 (0)**	**2.08**	**-463.91813 (0)**	**1.39**	- [c]	-	- [c]	-
B $C_{2h}{}^y$ (^2B_u)	-464.05759 (2)	3.65	-464.03234 (3)	3.36	-463.91702 (2)	2.09	-462.761838	4.97	-462.787425	3.54
b C_1 (^2A)	-464.05794 (1)	3.43	-464.03274 (1)	3.12	-463.91717 (1)	1.99	-462.762003	4.87	- [d]	-
G $C_s{}^{xz}$ ($^2A'$)	-464.05875 (1)	2.93	-464.03365 (1)	2.54	-463.91763 (1)	1.70	-462.763626	3.85	-462.789007	2.55
transition between domains										
TS C_2 (^2B)	-464.05782 (1)	3.49	-464.03256 (1)	3.23	-463.91657 (1)	2.7	-462.762566	4.52	-462.787708	3.36

[a] Data related to the PES minima are marked with bold.
[b] Number of imaginary vibrational frequencies.
[c] Non-stationary structure at this level of calculations (geometry optimization leads to restoring of C_{2h} symmetry).
[d] We failed to find the structure at this level of calculations. The search of TS did not converge, however, the C_{2h} symmetry did not restore.

3. Degenerate transformations of the orbital isomeric structures of the benzene dimer radical cation. The data of DFT calculations

Fig. S2 shows the sections of the PES of $(C_6H_6)_2^{+\cdot}$ along the internal reaction coordinates (IRCs) for the degenerate transformations $\mathbf{a} \leftrightarrow \mathbf{a'}$. The upper part of the figure relates to the transformation passing through transition state (TS) $\mathbf{D}$. The reaction coordinate is the relative rotation of the benzene rings. As one can see from Fig. S2a, it is the rotation that occurs at the first stage of the transformation. At the point marked with a cross, the gradient values are close to zero. If calculations are carried out with the standard accuracy, this point is the terminal point. It is defined as a minimum. However, further optimization of the geometry of the structure corresponding to the point, or IRC calculations with increased accuracy indicate that the marked point is an inflection point. After the point, the relative rotation of the rings is replaced by their shift relative to each other, and only in the last process does the electronic state of the system change, and we get another orbital isomer, structure $\mathbf{a}$. According to the notation introduced in the article, Fig. S1a depicts structure $\mathbf{a}(1\text{-}1')$. Moving in the opposite direction of the reaction coordinate will lead to the structure $\mathbf{a}(6\text{-}6')$. For comparison, a hypothetical situation is shown in the box when the transformation $\mathbf{D} \rightarrow \mathbf{a}$ occurs without changing the type of the reaction coordinate. If only the relative rotation of the rings occures, as was assumed in [1], the result is other versions of the structures $\mathbf{a}$, namely $\mathbf{a}(6\text{-}1')$ and $\mathbf{a}(1\text{-}6')$.

Fig. S1b relates to the transformation $\mathbf{a} \leftrightarrow \mathbf{a'}$ passing through TS $\mathbf{F}$. MO of one fragment of $\mathbf{F}$ initially corresponds to the SOMO of $\mathbf{a}$ (Fig. 5 in the article and Fig. S1b). The evolution of the electronic state of the second fragment causes a change in the relative position of the first, which can be interpreted as a movement around the second fragment (Fig. S1b). The variant of $\mathbf{F}$ shown in the figure is responsible for the conformational transformation $\mathbf{a}(1\text{-}1') \leftarrow \mathbf{F} \rightarrow \mathbf{a}(1\text{-}6')$.

The pathways of degenerate conformational transformations $\mathbf{c} \leftrightarrow \mathbf{c'}$ are shown in Fig. S3. The potential curve that connects $\mathbf{b}$ and $\mathbf{c}$ is depicted in the upper part of the figure. The reaction coordinate is the displacement of the benzene rings relative to each other. When moving along it, the type of SOMO changes. The IRC calculation does not lead to the local minimum $\mathbf{c}$. The final structure, marked in the curve with a red dot, differs from structure $\mathbf{c}$ by a larger angle of relative rotation of the fragments, but practically does not differ in energy. The extreme flatness of the PES in the vicinity of $\mathbf{c}$ does not allow changing the reaction coordinate and reaching this point. The curve shown in the Fig. S3a is a half-path of transformation $\mathbf{c}(1\text{-}1') \leftrightarrow \mathbf{c}(6\text{-}6')$.

For comparison, a hypothetical situation is shown in the box when the transformation $\mathbf{b} \rightarrow \mathbf{c}$ occurs as a result of the relative rotation of the rings, as suggested in [1]. Moving along the positive and negative directions of this coordinate leads to the structures $\mathbf{c}(6\text{-}1')$ and $\mathbf{c}(1\text{-}6')$.

The potential curve that connects **G** (TS) and **c** is depicted in Fig. S3b. As in the case of transformation **F** → **a**, in the TS of C_s symmetry, one of the fragments has the orbital structure that is necessary for the transition to a minimum. This fragment only adjusts to the change in the electron density distribution in the second fragment. The variant of TS shown in the figure corresponds to the conformational transition **c**(1-1') ↔ **c**(1-2').

Note that in the vicinity of both minima, the potential curves are extremely flat, which makes it practically impossible to determine accurately the angles of relative rotation of the fragments. For example, in the case of structure **a**, the angles obtained in geometry optimization and IRC calculations range from ~ 5 to ~ 30 degrees, while the corresponding values of the total energy coincide with an accuracy of <0.1 kcal / mol.
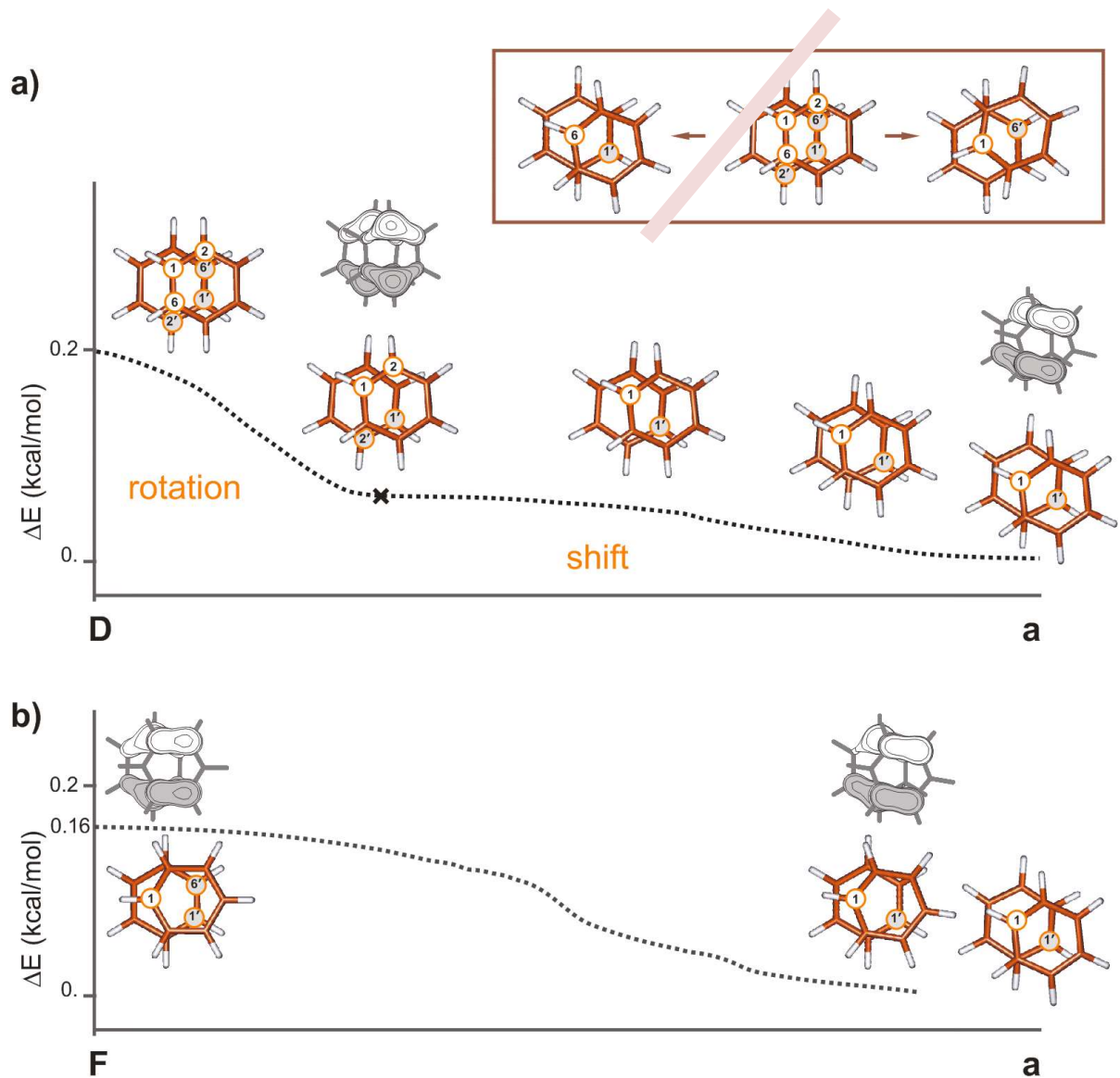
Figure S2. Sections of the PES of $(C_6H_6)_2^{+\cdot}$ along IRCs of transformations $\mathbf{D} \to \mathbf{a}$ (a) and $\mathbf{F} \to \mathbf{a}$ (b) (results of B3LYP-D3/6-31G* calculations). SOMO images for some chosen structures. In the frame: a hypothetical transformation $\mathbf{a} \leftarrow \mathbf{D} \to \mathbf{a'}$ through the relative rotation of the benzene rings. To indicate a variant of the structure, we give the numbers of several carbon atoms. The numbers with an apostrophe refer to the ring farther from the viewer.

Figure. S3. Sections of the PES of the $(C_6H_6)_2^{+\cdot}$ along IRCs of transformations $\mathbf{b} \rightarrow \mathbf{c}$ (a) and $\mathbf{G} \rightarrow \mathbf{c}$ (b) (results of B3LYP-D3/6-31G* calculations). SOMO images for some chosen structures. In the frame: a hypothetical transformation $\mathbf{c} \leftarrow \mathbf{b} \rightarrow \mathbf{c'}$ through the relative rotation of the benzene rings. To indicate a variant of the structure, we give the numbers of several carbon atoms. The numbers with an apostrophe refer to the ring farther from the viewer.
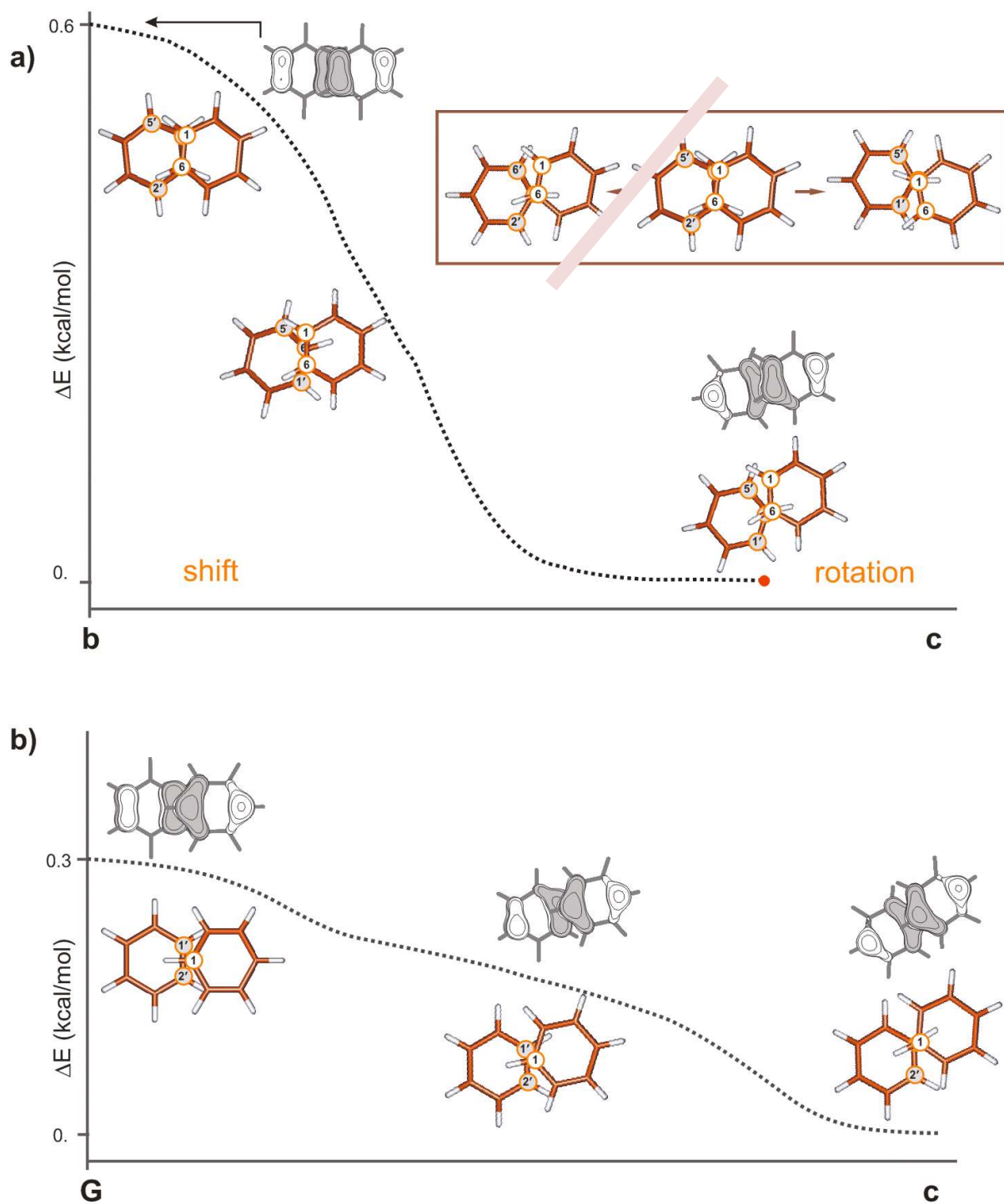
4. Comparison of potential energy profiles obtained in the B3LYP-D3/6-31G* and EOM-IP-CCSD/cc-pVDZ//B3LYP-D3/6-31G* approximations for the transformations of the stationary structures of $(C_6H_6)_2$
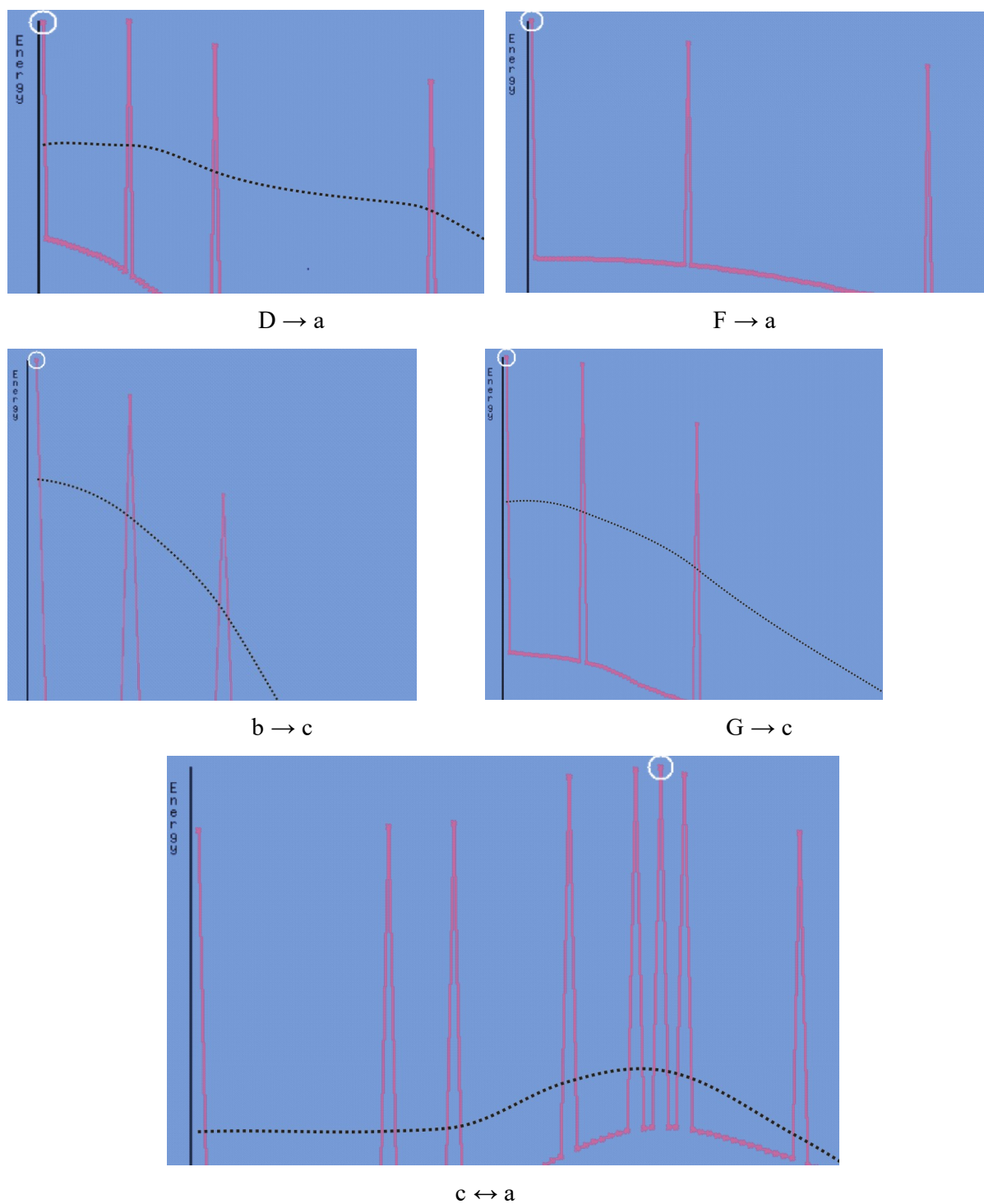

D → a

F → a

b → c

G → c

c ↔ a

Figure S4. Cross-sections of the PES along IRCs for various structural transformations of $(C_6H_6)_2^{+\bullet}$. Results of B3LYP and EOM-IP-CCSD//B3LYP calculations.

For selected points on the IRC, energy calculations were performed using the EOM-IP-CCSD method. The dotted line is the spike envelope shifted so that its minimum energy point coincides with the zero energy of the curve constructed at the B3LYP-D3 level. There is a qualitative similarity of the curves obtained by different methods.

5. Table S2. The averaged hfc constant with protons, $\bar{a}$ (12H), for the minimum energy structures[a)] of two orbital isomer of $(C_6H_6)_2^{+\bullet}$. Calculation using the B3LYP-D3/cc-pVDZ method.

geometry optimization method	structure	$\bar{a}$ (12H), G
	a	-2.15
B3LYP-D3/cc-pVDZ	**A**	-2.15
	c	-2.03
	a	-2.23
ωB97X-D/cc-pVDZ	**A**	-2.23
	c	-2.12
	A	-2.15
EOM-IP-CCSD/cc-pVDZ	**C**	-2.02

[a)] In the case of geometry optimization at the DFT level, calculations were carried out for the minimum energy structure **a** and its precursor structure **A**.

According to the calculations, the average hfc constant with protons ā (12H), estimated from the parameters of the minimum energy structures (**A** or **a**) of the first orbital isomer of $(C_6H_6)_2^{+\bullet}$, reveals a weak dependence on the method by which the geometry was optimized, however, in all cases, its calculated value falls within the range of experimental estimates (-2.15 — -2.24 G [2]). In this case, the constant does not depend on what symmetry (C_{2h}^x or C_2^x) the discussed structure has. The value of ā (12H) for the **C** (**c**) structure corresponding to the second orbital isomer of $(C_6H_6)_2^{+\bullet}$ is noticeably lower and does not fall within the range of experimental estimates at all levels of calculations.

6. References

1. A. Błoch-Mechkour, T. Bally, *Phys. Chem. Chem. Phys.*, 2015, **17**, 10624.
2. Y. Itagaki, N. P. Benetis, R. M. Kadam, A. Lund, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2683.

7. Cartesian coordinates for structures first described in this work, F, G, TS. (GAMESS, B3LYP-D3/6-31G*, angs)

F, U-B3LYP ENERGY IS   -463.920090

C_s (Only coordinates of symmetry unique atoms are given.)

C	-0.0297732809	-0.0390762902	0.6909462497
C	0.0199401845	1.1926235479	1.3900124233
C	0.0287345097	2.4199644686	0.6927909727
C	3.1620873142	0.7229780163	0.0000000000
C	3.1553805265	1.4269595048	1.2018974491
C	3.1938923027	2.8521776308	1.2014643862
C	3.2287367743	3.5579212741	0.0000000000
H	3.1553668187	-0.3618059210	0.0000000000
H	3.1685082993	0.8963586678	2.1492960458
H	3.2147512792	3.3823425395	2.1493594839
H	3.2756469430	4.6423120474	0.0000000000
H	-0.0683686252	-0.9712003962	1.2461714539
H	0.0085711148	1.1922402565	-2.4764943654
H	0.0254447644	3.3535073622	1.2461036400

G, U-B3LYP ENERGY IS   -463. 917630

C_s (Only coordinates of symmetry unique atoms are given.)

C	0.3915396600	-0.1956485421	0.0000000000
C	1.0937529842	-0.1220682581	1.2318804107
C	2.4730905363	-0.0017951699	1.2277763107
C	3.1647218275	0.0559162895	0.0000000000
H	0.5395648916	-0.1495705305	2.1647749830
H	3.0248565360	0.0600556107	2.1605895128
H	4.2463064440	0.1582937479	0.0000000000
H	-0.6923693976	-0.2429900221	0.0000000000
C	0.0201907256	-2.9810019372	0.7141093908
C	-1.1887717527	-2.9350533778	1.4172700497
C	-2.3854911992	-2.8874036005	0.7099622681
H	-1.1904547761	-2.9510051708	2.5027143323
H	-3.3325757053	-2.8607853959	1.2410307612
H	0.9640384928	-3.0568579066	-1.2438942677

TS, U-B3LYP ENERGY IS   -463.916570

C_2 (Only coordinates of symmetry unique atoms are given.)

C	-1.3670954842	-0.3024857897	1.0294460175
C	-1.9566256741	0.9425095383	1.3262884934
C	-2.5280257464	1.6833708750	0.3041326498
C	-2.5175552209	1.1905384396	-1.0256209115
C	-1.9226478366	-0.0384803228	-1.3304329566

```
C    -1.3372630866  -0.7825161577  -0.3126083244
H    -1.0069044537  -0.9401397017   1.8302804602
H    -1.9869793703   1.2978406135   2.3517498985
H    -3.0051254736   2.6353354182   0.5167894291
H    -2.9775678764   1.7792259226  -1.8142974295
H    -1.9178519322  -0.4051241202  -2.3519858519
H    -0.8606862668  -1.7347705064  -0.5236414745
```

8. Cartesian coordinates for stationary structures of $(C_6H_6)_2^{+\cdot}$ (Orca, EOM-IP-CCSD/cc-pVDZ, angs)

Structure **A**, E = -462.793065

```
C    2.017972   -1.466440    0.000001
C   -2.017972    1.466436   -0.000001
C    1.305896   -1.470732    1.208700
C   -1.305896    1.470730   -1.208699
C    1.305895   -1.470731   -1.208698
C   -1.305895    1.470728    1.208698
C   -0.126003   -1.516811    1.209221
C    0.126003    1.516811   -1.209221
C   -0.126004   -1.516810   -1.209219
C    0.126004    1.516810    1.209219
C   -0.832704   -1.578490    0.000001
C    0.832704    1.578491   -0.000001
H    3.112264   -1.456121    0.000001
H   -3.112264    1.456115   -0.000000
H    1.841741   -1.464332    2.164737
H   -1.841740    1.464331   -2.164737
H    1.841740   -1.464331   -2.164735
H   -1.841739    1.464326    2.164736
H   -0.659046   -1.575035    2.165129
H    0.659045    1.575038   -2.165129
H   -0.659046   -1.575035   -2.165127
H    0.659046    1.575035    2.165127
H   -1.924064   -1.656795    0.000001
H    1.924063    1.656799   -0.000002
```

Structure **B**, E = -462.787425

```
C   -0.153203   -1.411006   -0.717345
C    0.153203    1.411006    0.717345
C   -0.153203   -1.411006    0.717345
C    0.153203    1.411006   -0.717345
C   -1.370415   -1.483724    1.425871
C    1.370415    1.483724   -1.425871
C   -1.370415   -1.483724   -1.425871
```

```
C    1.370415    1.483724    1.425871
C   -2.571897   -1.548126    0.713793
C    2.571897    1.548126   -0.713793
C   -2.571897   -1.548126   -0.713793
C    2.571897    1.548126    0.713792
H    0.802117   -1.423708    1.252784
H   -0.802117    1.423708   -1.252785
H    0.802117   -1.423708   -1.252785
H   -0.802117    1.423708    1.252784
H   -1.369565   -1.506126    2.520346
H    1.369565    1.506126    2.520346
H   -1.369565   -1.506126   -2.520346
H    1.369565    1.506126    2.520346
H   -3.525007   -1.615552    1.249345
H    3.525007    1.615552   -1.249345
H   -3.525007   -1.615552   -1.249345
H    3.525007    1.615552    1.249345
```

Structure **C**, E = -462.789738

```
C   -1.316516    0.038631    0.000000
C    1.316516   -0.038631    0.000000
C   -1.391390    0.746639    1.238287
C    1.391390   -0.746639   -1.238287
C   -1.391390    0.746639   -1.238287
C    1.391390   -0.746639    1.238287
C   -1.488912    2.137624    1.233820
C    1.488912   -2.137624   -1.233820
C   -1.488912    2.137624   -1.233820
C    1.488912   -2.137624    1.233820
C   -1.532692    2.832712   -0.000000
C    1.532692   -2.832712   -0.000000
H   -1.385952    0.187851    2.180130
H    1.385952   -0.187851   -2.180130
H   -1.385952    0.187851   -2.180130
H    1.385952   -0.187851    2.180130
H   -1.549403    2.693154    2.175006
H    1.549403   -2.693154   -2.175007
H   -1.549403    2.693154   -2.175007
H    1.549403   -2.693154    2.175006
H   -1.619530    3.925028   -0.000000
H    1.619530   -3.925028   -0.000000
H    1.313934    1.057517    0.000000
H   -1.313934   -1.057517    0.000000
```

Structure **D**, E = -462.792829

```
C   -0.635197   -1.566282    0.698265
C    0.635197    1.566282   -0.698265
```

```
C   -0.635197   -1.566282   -0.698265
C    0.635197    1.566282    0.698265
C    0.595664   -1.488351   -1.397369
C   -0.595664    1.488351    1.397369
C    0.595664   -1.488351    1.397369
C   -0.595664    1.488351   -1.397369
C    1.836764   -1.459127   -0.694989
C   -1.836764    1.459127    0.694989
C    1.836764   -1.459127    0.694989
C   -1.836764    1.459127   -0.694989
H   -1.572814   -1.653134   -1.256940
H    1.572814    1.653134    1.256940
H   -1.572814   -1.653134    1.256940
H    1.572814    1.653134   -1.256940
H    0.598030   -1.507315   -2.493747
H   -0.598030    1.507315    2.493747
H    0.598030   -1.507315    2.493747
H   -0.598030    1.507315   -2.493747
H    2.776779   -1.445094   -1.256188
H   -2.776779    1.445094    1.256188
H    2.776779   -1.445094    1.256188
H   -2.776779    1.445094   -1.256188
```

Structure F, E = -462.792870

```
C   -0.009763   -0.054696   -0.695031
C   -0.009711   -0.054751    0.694988
C    0.064661    1.184392   -1.397505
C    0.064698    1.184322    1.397502
C    0.088963    2.417348   -0.698189
C    0.088971    2.417311    0.698227
C    3.105564    0.723221    0.000029
C    3.097254    1.432860   -1.208964
C    3.097232    1.432910    1.208996
C    3.162815    2.864202   -1.208482
C    3.162788    2.864254    1.208457
C    3.213884    3.574734   -0.000026
H    3.099792   -0.370906    0.000054
H    3.116463    0.897433   -2.165019
H    3.116430    0.897526    2.165076
H    3.196430    3.398554   -2.164804
H    3.196383    3.398649    2.164756
H    3.290294    4.666396   -0.000051
H   -0.070189   -0.992997   -1.256042
H   -0.070116   -0.993079    1.255953
H    0.045533    1.183884    2.493815
H    0.045488    1.183973   -2.493818
H    0.081057    3.358852   -1.256971
H    0.081058    3.358792    1.257048
```

Structure **G**, E = -462.789007

```
C    0.360657   -0.272742    0.000000
C    1.064708   -0.172450   -1.239834
C    1.064708   -0.172450    1.239834
C    2.449290   -0.015010   -1.235233
C    2.449290   -0.015010    1.235233
C    3.141381    0.061256   -0.000000
H    0.505849   -0.204100   -2.181099
H    0.505849   -0.204100    2.181099
H    3.002928    0.067614   -2.175800
H    3.002928    0.067614    2.175800
H    4.228756    0.196846   -0.000000
H   -0.734079   -0.319490    0.000000
C    0.056270   -2.970306   -0.715926
C    0.056270   -2.970306    0.715926
C   -1.162159   -2.903150   -1.424437
C   -1.162159   -2.903150    1.424437
C   -2.363920   -2.829814   -0.713081
C   -2.363920   -2.829814    0.713081
H   -1.164436   -2.928288   -2.518954
H   -1.164436   -2.928288    2.518954
H   -3.318042   -2.789042   -1.249540
H   -3.318042   -2.789042    1.249540
H    1.004457   -3.086081    1.252476
H    1.004457   -3.086081   -1.252476
```

Structure **TS**, E = -462.787708

```
C    0.045871   -1.471758   -0.352209
C   -0.045740    1.471207   -0.350386
C    0.433413   -1.288196    1.014453
C   -0.433893    1.288933    1.016266
C    1.803024   -1.166173    1.358202
C   -1.803609    1.167473    1.359487
C    2.767293   -1.250261    0.354616
C   -2.767418    1.250849    0.355352
C    2.378348   -1.460396   -1.001994
C   -2.377896    1.459734   -1.001304
C    1.024575   -1.570213   -1.353818
C   -1.024015    1.568989   -1.352591
H   -1.018280   -1.559913   -0.599694
H    1.018527    1.558981   -0.597514
H    0.734076   -1.732960   -2.396475
H   -0.732952    1.730753   -2.395242
H    3.151562   -1.539021   -1.774231
H   -3.150779    1.537818   -1.773920
H    3.831192   -1.180815    0.604630
```

```
H    -3.831436    1.181783    0.604965
H     2.096323   -1.041877    2.405716
H    -2.097442    1.044110    2.406962
H    -0.327547   -1.347187    1.800103
H     0.326804    1.348139    1.802168
```