

Theoretical study of substituent effects on the geometry and strain enthalpy in [2,2]paracyclophanes

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Abstract: The substituent effect on the geometry and strain enthalpy of [2,2]paracyclophane is theoretically investigated by density functional theory. Gas-phase calculations were performed for twenty distinct electron donating and electron withdrawing substituents. The largest out-of-plane distortion of phenyl rings is exhibited by —SCN and —CF₃ groups. On the other hand, —OH, —CH₃ and —F groups show the minimal deformation. The strain enthalpy for unsubstituted [2,2]paracyclophane associated with repulsive forces between phenyl units reached up to 118.5 kJ mol⁻¹. Any substitution causes increase of the strain enthalpy value proportionally to the absolute values of Hammett *para*-substituent constants. Two separate linear dependences with similar slopes were obtained for monosubstituted as well as double symmetrically substituted derivatives.

Keywords: Paracyclophane, B3LYP-D3 study, intermolecular forces, aromaticity, strain enthalpy, Hammett constants

Introduction

Aromatic molecules are among the most important classes of the compounds having a crucial role in biochemistry and material chemistry (Morisaki et al., 2010). It is well known that the relative orientation and distance between the aromatic rings in the solid state affects the electronic delocalization and therefore important bulk properties. For example, the face-to-face orientation of π -electron systems stacks the double-stranded main chains of DNA or it modulates the performance of various organic optoelectronic devices (Hinoue et al., 2012). The one of many long-standing challenges for chemists designing and constructing new organic materials is to understand quantitatively the physical and chemical properties of aromatic rings which are compressed face-to-face. In this context, the paracyclophanes represent the unique compounds having very specific structure (Boyd, 1966). These hydrocarbons often consist of benzene rings and aliphatic chains forming a bridge between two non-adjacent positions of the aromatic ring. The [n,n]paracyclophanes with shorter aliphatic chains possess considerably deformed aromatic rings from the planarity compared to the usual aromatic rings (Bachrach, 2011; Dodziuk et al., 2011). These deformations from the ideal aromatic geometry reflect the strong π - π electron repulsions between the two aromatic rings. As a result, increased π -electron density is found on the outside faces (Grimme, 2004). Needless to say, the largest nuclear repulsion occurs in [2,2]paracyclophane due to the shortest

distance between two benzene rings (C1...C7 and C4...C10, see Scheme 1). The experimentally determined distance is 2.780 Å, which is not only considerably less than the separation distance between the stacked aromatic molecules but also less than the sum of two carbon atoms van der Waals radii, *ca.* 3.4 Å. Until very recently, as discussed in detail in previous studies (Dodziuk et al., 2012), different experimental studies of [2,2]paracyclophane gave conflicting structural information, with X-ray data measured at 100 K yielding an eclipsed D_{2h} geometry (Lyssenko et al., 2003) and a D₂ geometry at room temperature (Demissie et al., 2016). Also the C1—C2—C9—C10 twist angle for the D₂ symmetry has been the subject of controversy in both experimental and theoretical studies. However, a recent study by Wolf et al. (Wolf et al., 2014) resolved the conflicting data by providing X-ray structural parameters measured at temperatures ranging from 15 K to 260 K. The authors reported that [2,2]paracyclophane has a twist angle of 12.83 (4)° at 15 K, 10.7 (3)° at 45 K and 0.0° above 55 K. Thus, this result supports the heat-capacity study by Andrews and Westrum (Andrews and Westrum, 1970), in which a hump in the heat capacity curve around 50 K was observed, suggesting the existence of a phase transition at this temperature. Introduction of a substituent to the [2,2]paracyclophane has direct influence on the electronic space structure between the aromatic moieties. Sheehan and Cram (Sheehan and Cram, 1969) reported experimental studies of the influence of several substituents at one aromatic ring on the other unsubstituted ring.



R ₁ = R ₂									
—NMe ₂	—NH ₂	—OH	—OCH ₃	—CH ₃	—CH=CH ₂	—F	—SH	—Cl	—C≡CH
—NCS	—CHO	—COOH	—NC	—MeCO	—SCN	—CF ₃	—CN	—NO ₂	—NO

Scheme 1. Atom numbering and structure of a) monosubstituted (**S1**) and b) disubstituted (**S2**) [2,2]paracyclophanes.

Later, Cram and Cram (Cram and Cram, 1971) pointed out that the inclusion of an activating substituent at one aromatic ring may also activate the second aromatic ring. Among the theoretical studies of substituted paracyclophanes, noteworthy is the work of Salcedo et al. (Salcedo et al., 2003). Using the density functional theory, authors showed that the mono and double substitution of [2,2]paracyclophane with three different groups, i.e. —NO₂, —OH and —CN, suffers the twist distortion and the electron population of the aromatic rings. The inductive effect has normal behaviour on the ring bearing the substitution, but it completely changes the behaviour of the counterpart ring confirming the proposition of Cram and Cram. In the case of the paracyclophanes, the substitution effect was theoretically explained by comparing with the geometrical changes and the changes of selected Nuclear Independent Chemical Shifts.

With respect to available published studies, we will present the quantum chemical calculations of the mono and symmetrically double substituted [2,2]paracyclophanes (Scheme 1) with 20 substituents showing various electron-donating and electron-withdrawing effects. The primary aim of this study is: (1) to provide a basic geometrical characterization of investigated molecules; (2) to evaluate the strain enthalpy quantifying the effect of a substituent on the repulsive forces between the phenyl rings; and (3) to examine the possible usage of Hammett constants for the correlation with the obtained theoretical data (Hammett 1937). The Hammett constants, originally designed as the descriptor of reaction rates and equilibrium constants of benzoic acid derivatives with *meta*- and *para*-substituents, are often successfully used as descriptors for various intramolecular properties and quantities. The possible utilisation of these constants for the estimation

of the substitution effect in [2,2]paracyclophanes was not presented in the literature yet.

Computational details

Quantum-chemical calculations were performed using the *Gaussian 09* program package (Frisch et al., 2009). All geometries were fully optimized in the gas phase by minimizing the energy with respect to all geometrical variables using the Density Functional Theory (DFT). The B3LYP-D3 functional with empirical Grimme's D3 dispersion and Becke-Johnson damping function was used without any constraints (Becke, 1993; Lee et al., 1988; Grimme et al., 2011; Frisch et al., 2009). The energy cut-off of 10⁻⁵ kJ mol⁻¹ was applied and the final RMS energy gradient was below 0.01 kJ mol⁻¹ Å⁻¹. For the species having several conformers all the conformers were investigated and the conformers with the lowest electronic energy were used. All calculations were performed using the standard 6-311++G(d,p) basis set for all atoms (Pople et al., 1980). The optimized structures were confirmed to be true minima by the vibration analysis (no imaginary frequency). Enthalpies were calculated for 298.15 K.

Results and Discussion

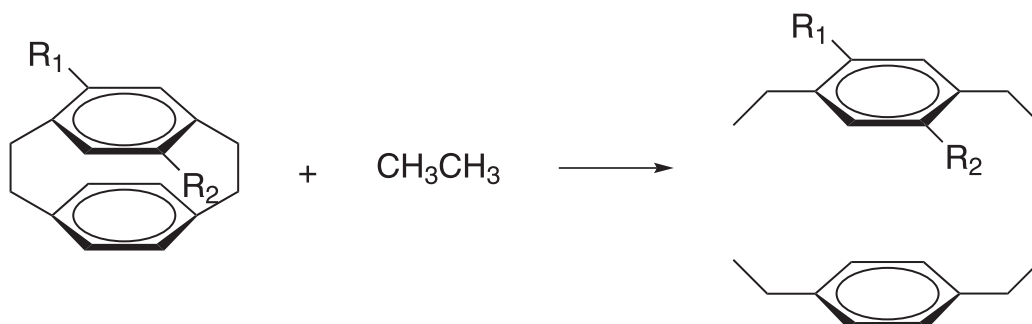
The optimal B3LYP-D3 geometry of [2,2]paracyclophane (**pC—H**) exhibits a slightly twisted structure (see Fig. 1), which is in accordance with published theoretical data (Demissie et al., 2016). The dihedral angle θ between C3—C6—C11 and C6—C11—C14 planes is of 3.9° and represents the mutual twist of phenyl rings. The data for the studied derivatives collected in Table 1 reveal that the dihedral angle θ is changed minimally. The largest deviation interval from -6.8° to -2.8° is present for

Tab. 1. B3LYP-D3/6-311++G(d,p) C1—C2/C9—C10 bond distances and dihedral angles θ for mono- (**S1**) and di-substituted (**S2**) paracyclophanes.

Substituent	H ₂ C—CH ₂ bond distance/Å		Dihedral angle θ /°	
	S1	S2	S1	S2
—NMe ₂	1.589/1.604	1.598/1.598	5.3	-6.5
—NH ₂	1.595/1.604	1.599/1.599	5.0	-6.5
—OH	1.596/1.606	1.590/1.590	4.3	-5.9
—OCH ₃	1.597/1.607	1.595/1.595	3.2	-6.0
—CH ₃	1.601/1.604	1.598/1.598	3.8	-4.3
—CH=CH ₂	1.596/1.604	1.597/1.597	4.7	-6.8
—H	1.604/1.604	1.604/1.604	3.9	3.9
—F	1.599/1.606	1.601/1.601	4.1	-5.7
—SH	1.596/1.604	1.600/1.600	4.7	-5.7
—Cl	1.599/1.604	1.595/1.595	4.5	-5.7
—C≡CH	1.599/1.605	1.598/1.598	4.7	-5.5
—NCS	1.600/1.607	1.600/1.600	3.9	-5.8
—CHO	1.595/1.603	1.594/1.594	4.8	-6.4
—COOH	1.595/1.603	1.593/1.593	4.3	-4.7
—NC	1.600/1.606	1.601/1.601	4.5	-5.6
—MeCO	1.595/1.603	1.594/1.594	3.6	-3.8
—SCN	1.596/1.604	1.595/1.595	4.4	-5.8
—CF ₃	1.603/1.601	1.603/1.603	3.9	-2.8
—CN	1.600/1.603	1.602/1.602	5.1	-5.2
—NO ₂	1.595/1.604	1.596/1.596	3.1	-2.9
—NO	1.597/1.602	1.596/1.596	5.3	-6.2

the double substituted moieties. Interestingly, the symmetric double substitution is responsible for small increase of the dihedral angle θ . The substitution has also the limited influence on the distances between C1—C2 and C9—C10 single bonds. These B3LYP-D3 distances for the parental **pC—H** molecule are of 1.604 Å. The mono substitution leads to the relevant decrease of this bond length at the site of added substituent. The minimal distance of 1.589 Å was observed for the —NMe₂ group. In the case of the symmetric double substitution on the same phenyl ring, the presence of —CN

and —CF₃ groups has the negligible influence on bond lengths. The close distance between the phenyl rings precludes the hydrogen atoms from being so near in a way that causes the distortion. The distances between the bridgehead carbons C3...C14 and C6...C11 on opposing rings for **pC—H** are of 2.798 Å while the distances between rings measured from the non-bridging carbon-carbon bonds are of 3.102 Å. The corresponding X-ray distances are of 2.782(1) Å and 3.097(2) Å, respectively (Lyssenko et al., 2003). The influence of the substitution on these interatomic distances can



Scheme 2. Investigated theoretical homodesmotic reaction scheme used for the evaluation of E_{str} enthalpies. B3LYP-D3/6-311++G(d,p) enthalpy of ethane molecule is of 79.783237 hartree.

Tab. 2. Selected B3LYP-D3/6-311++G(d,p) C...C interatomic distances (in Å) for mono- (**S1**) and di-substituted (**S2**) paracyclophanes.

Substituent	σ_p	Mono-substituted						Di-substituted		
		C3...C14	C4...C15	C5...C16	C6...C11	C7...C12	C8...C13	C3...C14/ C6...C11	C4...C15/ C7...C12	C5...C16/ C8...C13
—NMe ₂	-0.83	2.810	3.108	3.084	2.792	3.115	3.116	2.805	3.117	3.112
—NH ₂	-0.66	2.790	3.074	3.069	2.792	3.110	3.105	2.790	3.085	3.085
—OH	-0.37	2.783	3.061	3.062	2.794	3.108	3.102	2.787	3.077	3.076
—OCH ₃	-0.27	2.781	3.052	3.057	2.793	3.109	3.102	2.787	3.072	3.077
—CH ₃	-0.17	2.795	3.126	3.116	2.794	3.089	3.086	2.794	3.113	3.101
—CH=CH ₂	-0.02	2.798	3.094	3.091	2.790	3.104	3.108	2.812	3.134	3.107
—H	0.00	2.798	3.102	3.102	2.798	3.102	3.102	2.798	3.102	3.102
—F	0.06	2.786	3.053	3.052	2.793	3.115	3.111	2.787	3.073	3.072
—SH	0.15	2.795	3.115	3.103	2.791	3.102	3.107	2.789	3.114	3.113
—CCH	0.23	2.789	3.088	3.087	2.793	3.104	3.103	2.785	3.090	3.089
—Cl	0.23	2.788	3.088	3.080	2.794	3.105	3.101	2.786	3.093	3.085
—NCS	0.38	2.785	3.062	3.064	2.792	3.112	3.111	2.782	3.072	3.079
—CHO	0.42	2.785	3.092	3.102	2.795	3.113	3.121	2.796	3.106	3.109
—COOH	0.45	2.787	3.095	3.096	2.793	3.114	3.121	2.785	3.108	3.119
—NC	0.49	2.785	3.071	3.069	2.791	3.110	3.108	2.780	3.076	3.077
—MeCO	0.50	2.781	3.089	3.099	2.793	3.112	3.123	2.779	3.105	3.122
—SCN	0.52	2.793	3.114	3.105	2.790	3.105	3.113	2.787	3.116	3.117
—CF ₃	0.54	2.796	3.152	3.129	2.788	3.076	3.074	2.789	3.136	3.106
—CN	0.66	2.790	3.090	3.087	2.791	3.108	3.110	2.782	3.088	3.090
—NO ₂	0.78	2.779	3.083	3.082	2.787	3.110	3.120	2.773	3.096	3.107
—NO	0.91	2.784	3.078	3.077	2.788	3.112	3.120	2.781	3.094	3.099

be deduced from the data presented in Table 2. In general, the C3...C14 and/or C6...C11 distances are shortened in the vicinity of the added group. On the other hand, the remaining C4...C15, C7...C12 and C5...C16, C8...C13 distances are mostly elongated. The greatest difference between the C3...C14/C6...C11 and the above remaining distances indicate the largest off-planarity of phenyl rings. It seems that the —MeCO, —SCN and —CF₃ groups cause the largest deformation of phenyl rings for the **S1** and **S2** substitution. On the other hand, the minimal deformation occurs in the case of —OH, —CH₃ and —F groups.

The repulsive forces between the phenyl rings in paracyclophane core are responsible for the deformation of phenyl rings and they can be characterised by the strain enthalpy. This enthalpy is associated with two regions of the molecule: the phenyl rings and the alkyl linkers. Distortion of the phenyl ring from planarity results in a loss of aromatic stabilization energy. The alkyl chains are strained mostly by potential eclipsing interactions. The evaluation of the ring strain enthalpy (E_{str}) requires the selection of appropriate reference compound according to the isodesmic reaction

presented in Scheme 2. In the work of Caramori et al. (Caramori et al., 2005), p-dimethylbenzene was suggested as the suitable reference compound. As mentioned by Bachrach (Bachrach, 2011), the computed strain enthalpy values (E_{str}) are dependent on the DFT functional and selected approach. For the **pC—H**, $E_{\text{str}}(\mathbf{pC—H})$ enthalpy can vary from 112.9 kJ mol⁻¹ (B-97D) to 190.6 kJ mol⁻¹ (Hartree-Fock). Our resulting B3LYP-D3/6-311++G(d,p) enthalpy is of 118.5 kJ mol⁻¹ and any substitution increases this value. The enthalpy differences ΔE_{str} evaluated with respect to the $E_{\text{str}}(\mathbf{pC—H})$

$$\Delta E_{\text{str}} = E_{\text{str}}(\mathbf{substituent}) - E_{\text{str}}(\mathbf{pC—H}) \quad (1)$$

are collected in Table 3. The mutual comparison of these values shows that the double substitution increases the ΔE_{str} values. The minimal strain is connected with the addition of the methyl group or fluorine atom. On the other hand, the maximal and comparable effect is indicated for the strong electron donating —NMe₂ group ($\Delta E_{\text{str}} = 16/28$ kJ mol⁻¹) and electron withdrawing —NO₂ group ($\Delta E_{\text{str}} = 13/25$ kJ mol⁻¹). The absence of the negative ΔE_{str} values indicate that even the

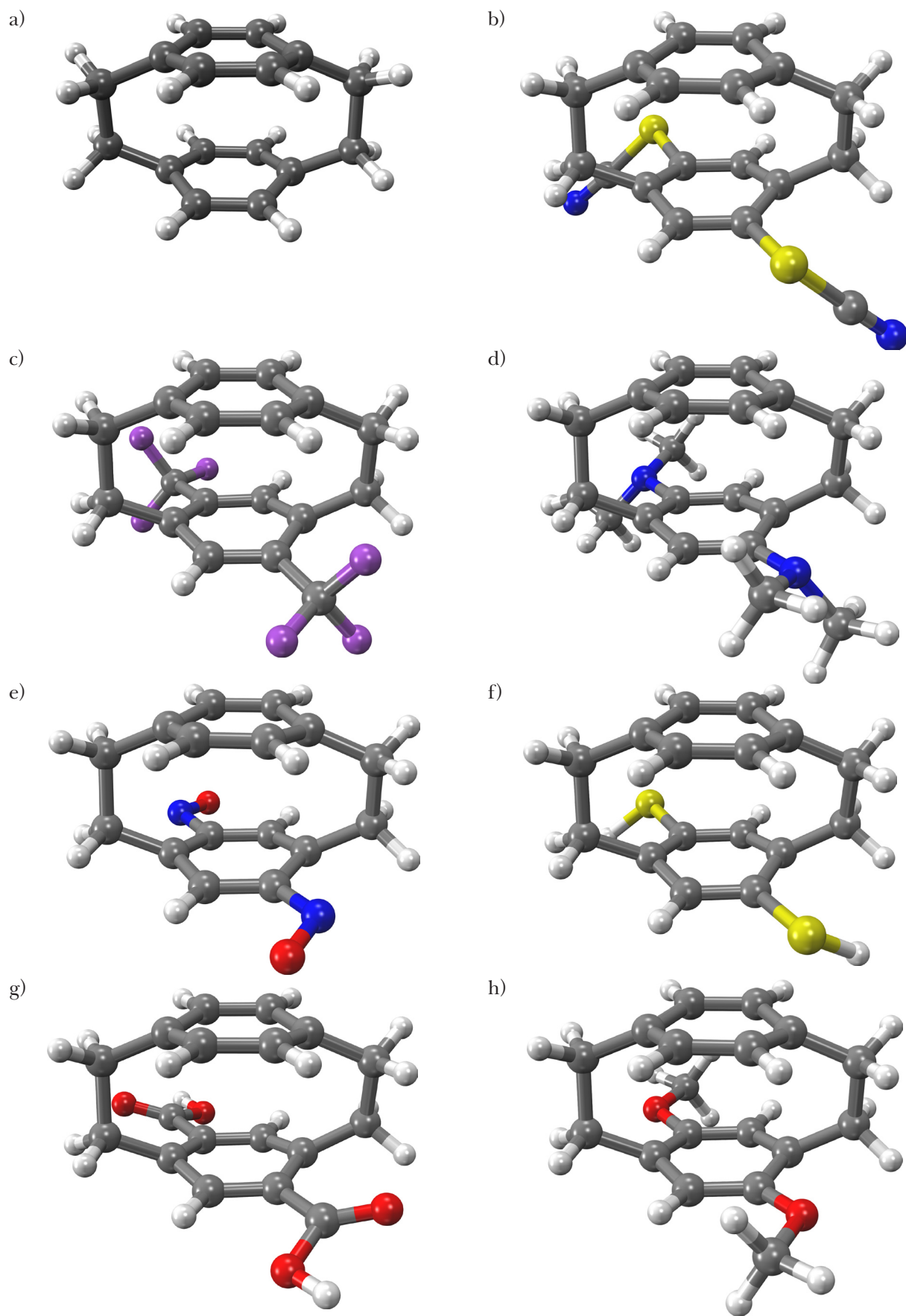


Fig. 1. B3LYP-D3/6-311++G(d,p) optimal geometries of non-substituted and selected disubstituted [2,2]paracyclophanes with $-\text{SCN}$, $-\text{CF}_3$, $-\text{NMe}_2$, $-\text{NO}_2$, $-\text{SH}$, $-\text{COOH}$ and $-\text{OCH}_3$ substituents (C – black, H – white, N – blue, O – red, F – violet, S – yellow) .

Tab. 3. Hammett constants describing *para* (σ_p) and *meta* (σ_m) effects for the studied substituents. Relative B3LYP-D3/6-311++G(d,p) strain enthalpies (ΔE_{str}) for mono- (**S1**) and di-substituted (**S2**) paracyclophanes. The reference B3LYP-D3/6-311++G(d,p) strain enthalpy of [2,2]paracyclophane $E_{\text{str}}(\text{pC—H}) = 118.5 \text{ kJ mol}^{-1}$.

Substituent	σ_p	σ_m	$\Delta E_{\text{str}}/\text{kJ mol}^{-1}$	
			S1	S2
—NMe ₂	-0.83	-0.15	16.0	27.8
—NH ₂	-0.66	-0.16	8.7	16.2
—OH	-0.37	0.12	6.8	11.3
—OCH ₃	-0.27	0.12	9.1	15.2
—CH ₃	-0.17	-0.07	5.7	11.5
—CH=CH ₂	-0.02	0.05	8.6	4.6
—F	0.06	0.34	5.2	9.6
—SH	0.15	0.25	9.0	18.8
—CCH	0.23	0.21	7.5	14.8
—Cl	0.23	0.37	8.6	17.0
—NCS	0.38	0.48	10.6	19.8
—CHO	0.42	0.35	10.5	14.4
—COOH	0.45	0.37	12.1	23.8
—NC	0.49	0.48	8.4	16.5
—MeCO	0.50	0.38	13.4	27.3
—SCN	0.52	0.51	11.5	21.0
—CF ₃	0.54	0.43	7.5	13.8
—CN	0.66	0.56	8.0	16.1
—NO ₂	0.78	0.71	12.8	24.8
—NO	0.91	0.62	10.9	20.4

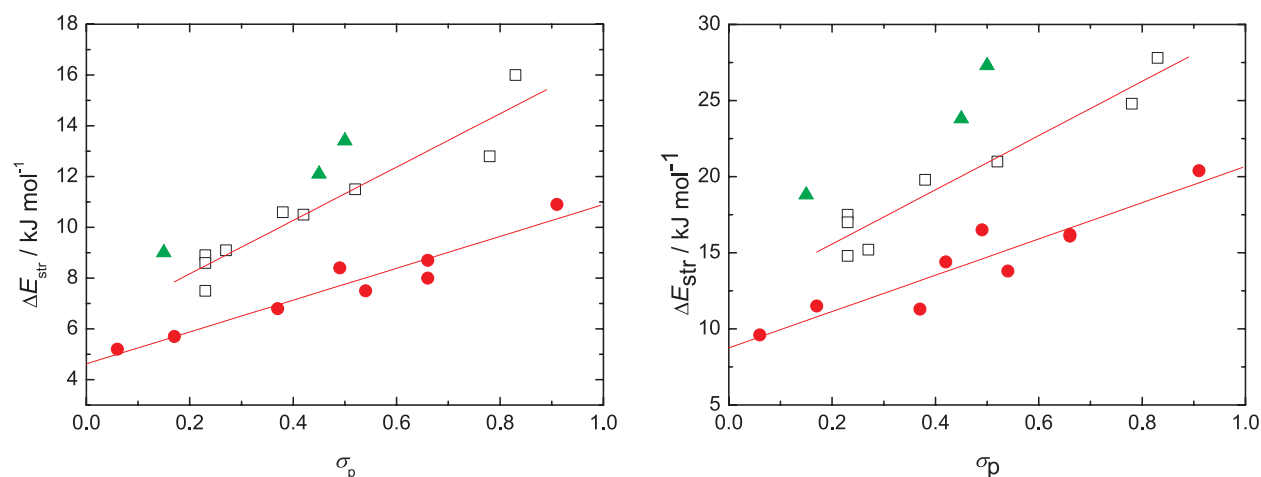


Fig. 2. The dependence of B3LYP-D3/6-311++G(d,p) ΔE_{str} energies on the absolute Hammett constant values of (a) mono- and (b) disubstituted [2,2]paracyclophanes for *para* effects (hollow squares – bulky substituents, red dots – small groups, green triangles – omitted substituents).

substitution with a small group is not able to electronically weaken the π - π stacking repulsion between phenyl rings comparing to the **pC—H** reference molecule. Otherwise, our theoretical calculations predict the aromaticity decrease upon the substitution with either electron-donating or with-

drawing groups. On the other hand, the absolute values of Hammett constants for *para* effects could be used for the description of the substitution effect. As it can be seen in Fig. 2a, two linear dependencies with the regression coefficients $R = 0.95$ and 0.96 were achieved for the mono

substituted molecules. From the linear regression, we obtained the following equations

$$\Delta E_{\text{str}} = 6.07(63) + 1.05(13) \cdot 10^1 \cdot |\sigma_p| \quad (2)$$

$$\Delta E_{\text{str}} = 4.62(40) + 6.27(73) \cdot |\sigma_p| \quad (3)$$

Eq. (2) was evaluated from the enthalpies corresponding to the relatively bulky groups or atoms. On the other hand, the second dependence contains eight relatively small substituents —CF₃, —CH₃, —CN, —F, —NC, —NH₂ and —NO. We have omitted three bulky substituents from the data evaluation, i.e. —SH, —COOH and —OCH₃ (see Fig. 1).

As it is shown in Fig. 2b, two linear dependences were also obtained for disubstituted derivatives

$$\Delta E_{\text{str}} = 12.01(98) + 1.78(19) \cdot 10^1 \cdot |\sigma_p| \quad (4)$$

$$\Delta E_{\text{str}} = 8.76(91) + 1.19(17) \cdot 10^1 \cdot |\sigma_p| \quad (5)$$

The slopes are approximately two-times larger than for the mono substituted derivatives. This indicates the additive character of the second substituent on the same phenyl ring. The values of their regression coefficients of 0.95 and 0.96, respectively, are statistically relevant. Interestingly, the second dependence contains 9 substituents, i.e. —CHO group was not involved in the Eq. (4).

Conclusions

In this work, we have investigated theoretically the substituent effect on the geometry and strain enthalpy of [2,2]paracyclophane core. The B3LYP-D3 calculations including long-range dispersion contributions were performed for 20 distinct electron donating or electron withdrawing substituents. The largest out-of-plane distortion of phenyl rings exhibit —MeCO, —SCN and —CF₃ groups. On the other hand, the minimal deformation is indicated for the —OH, —CH₃ and —F groups. The substituent effect on the repulsive forces between the phenyl units was associated with the strain enthalpy which was minimal for the [2,2]paracyclophane. The corresponding value of E_{str} enthalpy is 118.5 kJ mol⁻¹. Any substitution increases the values of this enthalpy. The minimal strain is connected with the addition of methyl group or fluorine atom. On the other hand, the maximal and comparable effect is indicated for the strong electron donating —NMe₂ group and electron withdrawing —NO₂ group. The evaluated strain enthalpies are rather dependent on the absolute values of Hammett constants for *para* effects than for the *meta* effects. Two separate linear dependences with similar slopes were obtained for the mono substituted as well as disubstituted deriva-

tives. The parameters of the dependencies are apparently also affected by the size of the substituent. Even the small groups are not able to electronically weaken the π - π stacking repulsion between phenyl rings comparing to the **pC—H** reference molecule. Future studies will be devoted to the investigation of the possible correlation of the NMR shifts as well as partial charges on atoms with Hammett constants.

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