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Intramolecular Hypervalent X←X Interaction in Heteropentalene Compounds Containing S and O Atoms*

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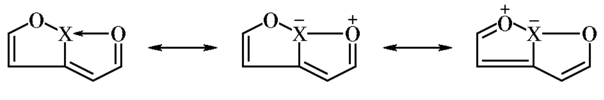
Abstract—Chalcogen-containing heteropentalene and quasimonocyclic compounds having O–O–O and S–S–S triads or O–O and S–S diads were studied by the *ab initio* [MP2(full)/6-31G** and MP2(fc)/6-31+G**] and DFT (B3LYP/6-31G**) methods. The oxygen-containing compounds are characterized by strong O···O repulsion which destabilize the pentalene structure. The molecule of 3-thioxo-1-propenesulfenyl fluoride, in contrast to 3-mercapto-2-propenethial, is more stable in the *cis-s-cis* conformation with an appreciably shortened S···S contact [2.274 Å (MP2), 2.503 Å (B3LYP)] which approaches the length of a standard S–S covalent bond.

According to both experimental and theoretical studies [1–4], chalcogen-containing 10π-electron pentalene compounds **Ia**–**Ic** have a planar C_{2v} structure with *T*-configuration of bonds at the chalcogen atom. This structure is stabilized by formation of a strong three-center four-electron (hypervalent) bond due to intramolecular attractive X←O interaction between the electron-rich centers:

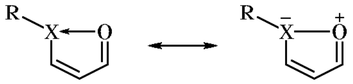


Ia **Ib** **Ic**

I, X = S (**a**), Se (**b**), Te (**c**).

The hypervalent X←O interaction results in considerable shortening of the X···O distance (2.043 Å for O···S, 2.085 Å for O···Se, and 2.172 Å for O···Te [3]) relative to the sum of the corresponding van der Waals radii (3.30 Å for O···S, 3.40 Å for O···Se, and 3.60 Å for O···Te [5]); the energy of the hypervalent X←O bond increases in the series S, Se, Te (O→S, 12.1 kcal/mol; O→Se, 19.8 kcal/mol; and O→Te, 27.7 kcal/mol [3]).

The energy of the X←O donor–acceptor interaction in monocyclic compounds **IIa**–**IIf** with a 6π-electron aromatic system also increases in the series O→S, O→Se, O→Te (5.0, 10.5, and 16.5 kcal/mol; R = Cl [1]). There are detailed published data, both experimental [1, 2] and theoretical [4], on chalcogen-containing pentalehe systems like **I** and **II** in which the electron-donor oxygen center is replaced by isoelectronic NR, S, or Se atom. However, no information is available on analogs of **I** having an O–O–O triad. A possible reason is that such compounds could be unstable since the hypervalent O–O–O bond is relatively weak or there exists a destabilizing repulsive interaction.



II **II′**

II, X = S, R = H (**a**); X = S, R = Cl (**b**); X = Se, R = H (**c**); X = Se, R = Cl (**d**); X = Te, R = H (**e**); X = Te, R = Cl (**f**).

The goal of the present work was to study intramolecular hypervalent O···O interaction in oxygen-containing pentalene (**IIIa**) and quasicyclic structures (**IVa**, **IVb**) and the possibility for their aromatic stabilization. We also planned to compare the results with those for related trithiapentalene (**IIIb**) and quasicyclic sulfur-containing structures (**IVc**, **IVd**).

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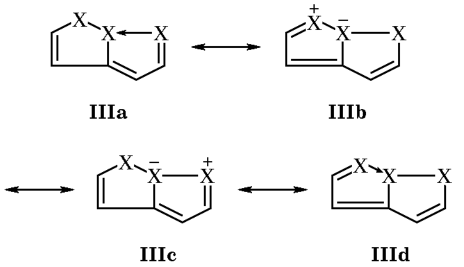
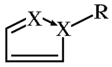


IIIa **IIIb** **IIIc** **IIId**

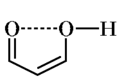


IVa–IVd

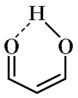
III, X = O (**a**), S (**b**); **IV**, X = O, R = H (**a**); X = O, R = F (**b**); X = S, R = H (**c**); X = S, R = F (**d**).

Calculation procedure. The calculations were performed in terms of the nonempirical Hartree–Fock (RHF) method with account taken of all (full) or only valence electrons (fc), according to the second-order Meller–Plesset perturbation theory (MP2), and in terms of the density functional theory (DFT, B3LYP) with the valence-split 6-31G** and 6-31+G** basis sets; Gaussian-94 [6] and GAMESS [7] software packages were used. Full geometry optimization of the molecular structures corresponding to stationary points (λ = 0 for minimal-energy points and λ = 1 for saddle points, where λ is the number of negative eigenvalues of the Hesse matrix in a given stationary point [8]) on the potential energy surface (PES) was run until a gradient value of 10^{-5} a.u./bohr (GAMESS software or the "tight" mode of Gaussian-94). The molecular structures shown in figures were plotted with the aid of PD program (PLUTO mode) of the PCMODEL software package [9].

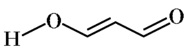
3-Hydroxy-2-propenal. According to the calculations, the enol form of malonaldehyde (3-hydroxy-2-propenal) is more stable in conformation **V** with intramolecular hydrogen bond [10, 11].



IVa

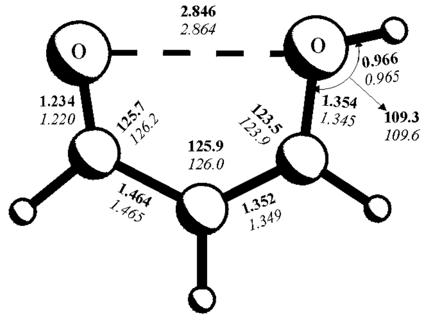


V

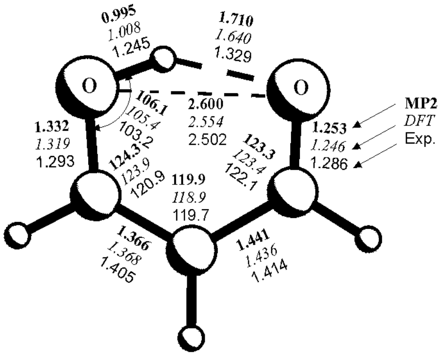


VI

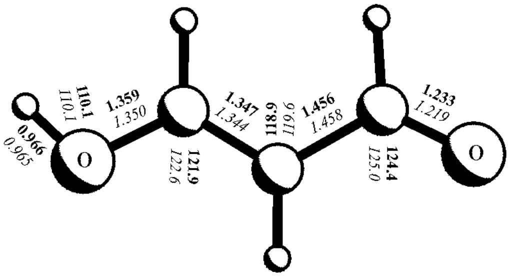
The *cis-s-cis*-structure of **IVa** also corresponds to a minimum (λ = 0) on the PES, but it is 12.9 (MP2) and 15.0 kcal/mol (B3LYP) less favorable than conformer **V**. The O···O distance in molecule **IVa** is 2.846 Å (MP2) or 2.864 Å (B3LYP); these values are very similar to the sum of standard van der Waals radii of two oxygen atoms (2.8 Å) [5]. Therefore, the O···O interaction in **IVa** is repulsive. In order to estimate the energy of the O···O interaction in **IVa** we calculated the corresponding *trans-s-trans*-structure of 3-hydroxy-2-propenal (**VI**) which lacks short O···O contact so that the oxygen atoms are distant from each other. Structure **VI** turned out to be by 4.5 (MP2) or 4.1 kcal/mol (B3LYP) more stable than structure **IVa**. The relative values of ΔE_{ZPE} and ΔH change only slightly when zero-point energy and temperature factors are taken into account. Thus, the



IVa, C_s, λ = 0



V, C_s, λ = 0



VI, C_s, λ = 0

Fig. 1. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IVa**, **V**, and **VI**, calculated by the MP2(fc)/6-31+G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers). The experimental data were taken from [12].

Table 1. Results of *ab initio* [(MP2(fc)/6-31+G**] and DFT (B3LYP/6-31G**) calculations of structures **IV–XI**[a]

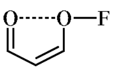
Structure no.	Method	λ	E_{tot}, a.u.	ΔE, kcal/mol	ZPE, a.u.	ΔE_{ZPE}, kcal/mol	ΔH, kcal/mol	ω, cm^{-1}
IVa	MP2	0	–266.396245	0	0.067250	0	0	115
	B3LYP	0	–267.135168	0	0.067003	0	0	162
V	MP2	0	–266.416806	–12.9	0.068523	–12.1	–12.5	259
	B3LYP	0	–267.159104	–15.0	0.067861	–14.5	–14.9	279
VI	MP2	0	–266.403439	–4.5	0.067267	–4.5	–4.5	139
	B3LYP	0	–267.141776	–4.1	0.066832	–4.3	–4.2	154
IVb	MP2	0	–365.287615	0	0.057507	0	0	38
	B3LYP	0	–366.247564	0	0.057285	0	0	74
VII	MP2	0	–365.292096	–2.8	0.057457	–2.8	–2.7	52
	B3LYP	0	–366.251320	–2.4	0.057012	–2.5	–2.4	82
VIII	MP2	1	–365.289114	–2.2	0.057218	–2.0	–1.6	i 108
	B3LYP	1	–366.251038	–2.2	0.056851	–2.5	–2.8	i 83
IVc	MP2	0	–911.577323	0	0.060966	0	0	97
	B3LYP	0	–913.072393	0	0.060216	0	0	147
IX	MP2	0	–911.578564	–0.8	0.059888	–0.9	–0.4	43
	B3LYP	0	–913.074349	–1.2	0.059323	–1.8	–1.4	120
IVd	MP2	0	–1010.603786	0	0.054820	0	0	70
	B3LYP	0	–1012.298977	0	0.053954	0	0	124
X	MP2	0	–1010.575421	17.8	0.053566	17.0	17.6	64
	B3LYP	0	–1012.276058	14.4	0.052762	13.7	14.2	43
XI	MP2	1	–1010.575427	17.8	0.053159	16.8	16.9	i 97
	B3LYP	1	–1012.276028	14.4	0.052624	13.6	13.6	i 25

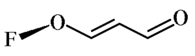
[a] λ is the number of negative Hessian eigenvalues for a given stationary point; E_{tot} and ΔE are, respectively, the total and relative energies (1 a.u. = 627.5095 kcal/mol); ZPE is the zero-point energy; ΔE_{ZPE} is the relative energy corrected for the zero-point energy; ΔH is the relative enthalpy; and ω is the minimal or imaginary harmonic frequency.

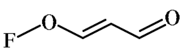
quantities ΔE, ΔE_{ZPE}, and ΔH can be regarded as qualitative estimates of the O···O repulsion. The calculated geometry and energy parameters of structures **IVa**, **V**, and **VI** are given in Fig. 1 and Table 1. The calculated geometric parameters of structure **V**, obtained in this work, are well consistent with the results of earlier theoretical studies [10] and experimental data [11] (Fig. 1).

In going from *cis-s-cis*-structure **IVa** to *trans-s-trans*-conformer **VI**, the C–C bond alternation almost does not change, i.e., the differences between the lengths of single and double carbon–carbon bonds in these structures are very similar: Δ*l*(R = H) = 0.111 Å (MP2), 0.116 Å (B3LYP) (**IVa**); Δ*l*(R = H) = 0.109 Å (MP2), 0.114 Å (B3LYP) (**VI**). This fact indirectly indicates the absence of aromatic stabilization of structure **IVa**.

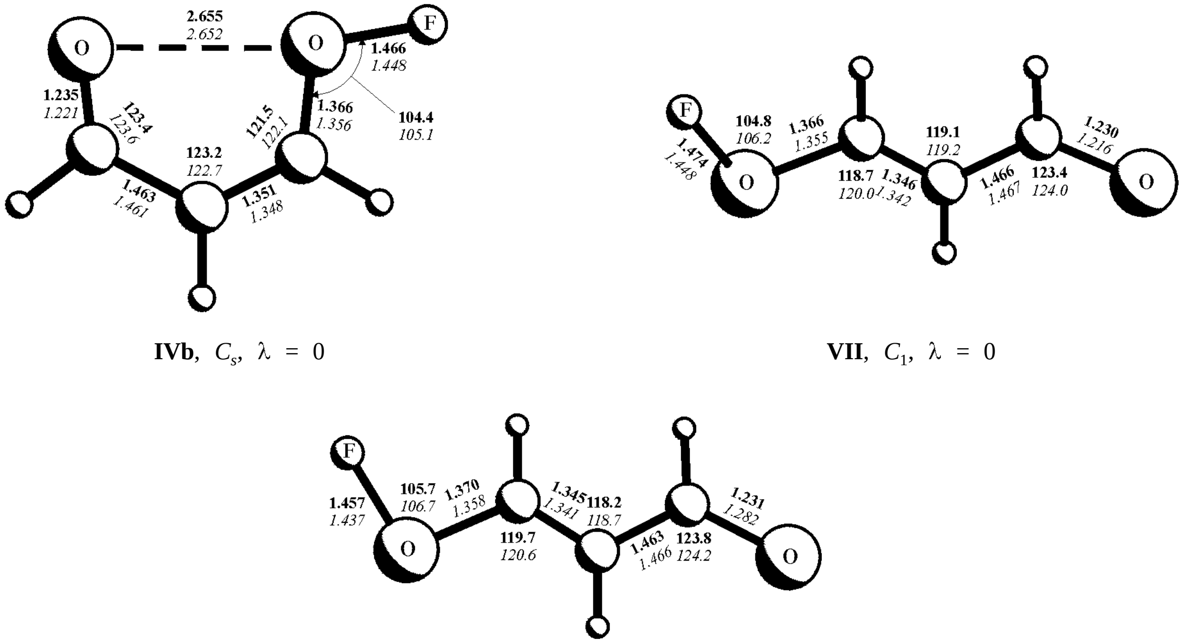
3-Fluoroxy-2-propenal. *cis-s-cis*-Structure **IVb** with a short O···O contact is a stable form of 3-fluoroxy-2-propenal, corresponding to an energy minimum (λ = 0) on the potential energy surface. The O···O distance in **IVb** [2.639 Å (MP2) or 2.652 Å (B3LYP)] is shorter than the sum of the standard van der Waals radii of oxygen atoms (2.8–3.2 Å) [5]. The corresponding *trans-s-trans*-structure **VII** also corresponds to an energy minimum on the PES and has no C_1 symmetry.


IVb


VII


VIII

Structure **VIII** has a C_s symmetry; it corresponds to a saddle point on the PES (λ = 1) and is a transition state for internal rotation of the O–F bond about the O–C bond with a barrier of 2.2 (MP2) or 2.2 kcal/mol (B3LYP). According to the calculations, structure **VII** is by 2.8 (MP2) or 2.4 kcal/mol



IVb, C_s, $\lambda = 0$

VII, C_1, $\lambda = 0$

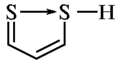
VIII, C_s, $\lambda = 1$

Fig. 2. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IVb**, **VII**, and **VIII**, calculated by the MP2(fc)/6-31+G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers).

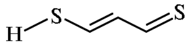
(B3LYP) more favorable than **IVb**; this indicates that the O···O interaction is also repulsive, though it is considerably weaker (by a factor of 2) than the interaction in **IVa**. The calculated geometry and energy parameters of structures **IVb**, **VII**, and **VIII** are given in Fig. 2 and Table 1.

The alternation of carbon–carbon bonds increases in going from *cis-s-cis*-isomer **IVb** to *trans-s-trans*-structure **VII**. The differences between the single and double bonds are as follows: **IVb**: Δl(R = F) = 0.112 Å (MP2), 0.113 Å (B3LYP); **VII**: Δl(R = F) = 0.120 Å (MP2), 0.125 Å (B3LYP). These data indicate a weak aromatic character of structure **IVb**.

3-Mercapto-2-propenethial. Unlike 3-hydroxy-2-propenal, the molecule of 3-mercapto-2-propenethial is stable only in the planar *cis-s-cis*-conformation **IVc** with a shortened S···S contact. A structure like **V** (with S···HS intramolecular hydrogen bond) does not correspond to a stationary point on the PES.



IVc



IX

Comparison of the total energies of structures **IVc** and **IX** indicates that the S···S interaction in **IVc** is

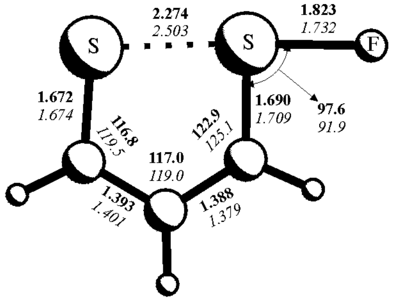
IVc, C_s, $\lambda = 0$

IX, C_s, $\lambda = 0$

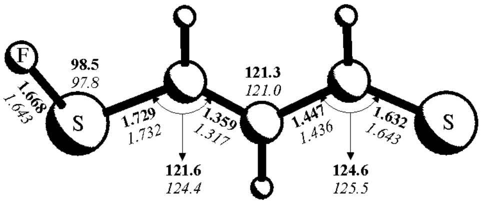
Fig. 3. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IVc** and **IX**, calculated by the MP2(fc)/6-31+G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers).

repulsive. On the other hand, the calculated S−S bond length in **IVc** is considerably smaller [3.129 Å (MP2), 3.137 Å (B3LYP)] than the sum of the standard van der Waals radii of sulfur atoms (3.7 Å) [5]. The calculated geometry and energy parameters of structures **IVc** and **IX** are given in Fig. 3 and Table 1. The alternation of carbon–carbon bonds in *cis-s-cis*-structure **IVc** is insignificant: the difference Δl between the single and double bond lengths is 0.072 Å (MP2) or 0.068 Å (B3LYP). *trans-s-trans*-Structure **IX** is characterized by a greater bond alternation: Δl 0.085 Å (MP2) or 0.081 Å (B3LYP). These results indicate higher aromaticity of structure **IVc** compared to **IVa**.

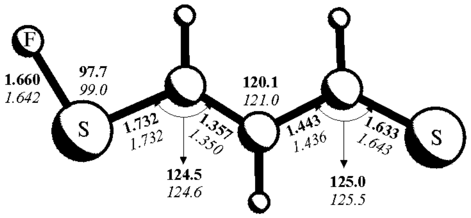
3-Thioxo-1-propenesulfenyl fluoride. The stable conformation of the molecule of 3-thioxo-1-propenesulfenyl fluoride is *cis-s-cis*-**IVd** with a strongly shortened S···S contact [2.274 Å (MP2), 2.503 Å (B3LYP)]. This distance is by almost 1.5 Å shorter than the sum of the corresponding van der Waals radii and only by 0.2–0.4 Å greater that the standard length of covalent S−S bond; for example, the S–S bond length in H_2S_2 is 2.055 Å [12]. Thus replacement of the hydrogen atom in the thiol group of **IVc** by more electronegative fluorine atom leads to formation of of strong three-center four-electron S−S−F bond in fluoride **IVd**. Presumably, the choice by the nature of sulfur atoms for formation of disulfide bridges to stabilize tertiary protein structure *in vivo* [13] is based on the ability of nonvalence S···S contact to be transformed into a strong S−S bond; this transformation is initiated by an electronegative reagent.



IVd, C_s, λ = 0



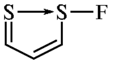
X, C_1, λ = 0



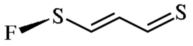
XI, C_s, λ = 1

Fig. 4. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IVd**, **X**, and **XI**, calculated by the MP2(fc)/6-31+G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers).

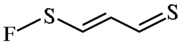
According to the calculations, *trans-s-trans*-structure **X** is by 17.8 (MP2) or 14.4 kcal/mol (B3LYP) less favorable than *cis-s-cis*-conformer **IVd**; these values can be regarded as a qualitative estimate of the energy of hypervalent S←S interaction. The calculated geometry and energy parameters of structures **IVd**, **X**, and **XI** are given in Fig. 4 and Table 1.



IVd



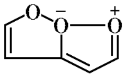
X



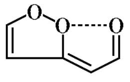
XI

There is almost no carbon–carbon bond alternation in *cis-s-cis*-structure **IVd**, as follows from the small Δl values: 0.005 Å (MP2), 0.022 Å (B3LYP). In going to *trans-s-trans*-structure **X**, Δl increases by about 0.1 Å: Δl = 0.088 Å (MP2), 0.119 Å (B3LYP).

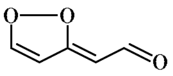
2-(3*H*-1,2-Dioxol-3-ylidene)acetaldehyde. The calculations showed that bicyclic pentalene structure **IIIa** with a C_{2v} symmetry corresponds to a saddle point on the potential energy surface and is the transition structure for O−O bond migration in the triad O−O···O $\rightleftarrows$ O···O−O: **XII** $\rightleftarrows$ **IIIa** $\rightleftarrows$ **XII**′.



IIIa

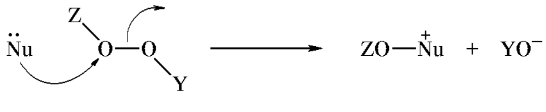


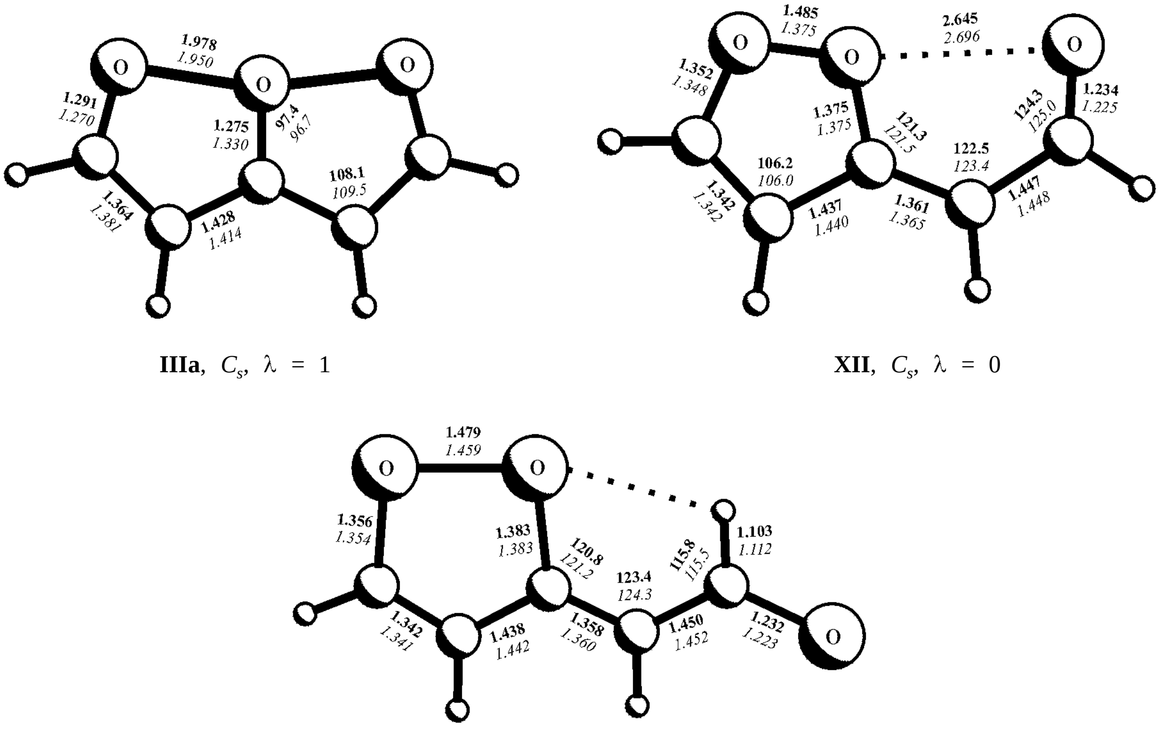
XII



XIII

This process follows the intramolecular nucleophilic substitution path (S_N2), involving the central oxygen atom and is characterized by a low activation barrier: 9.1 (MP2) or 7.8 kcal/mol (B3LYP).





IIIa, C_s, $\lambda = 1$

XII, C_s, $\lambda = 0$

XIII, C_s, $\lambda = 0$

Fig. 5. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IIIa**, **XII**, and **XIII**, calculated by the MP2(full)/6-31G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers).

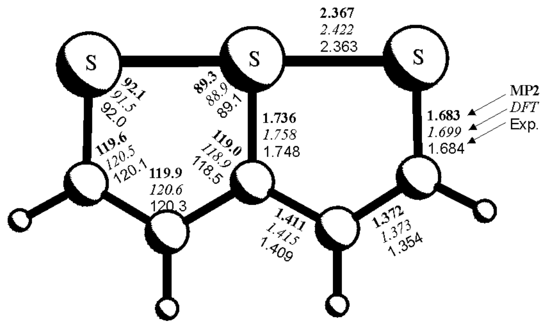
Unfortunately, we have found no experimental data on S_N2 intramolecular substitution at the oxygen atom, although a number of heterolytic oxidation reactions are likely to include an analogous step [14–16].

Planar monocyclic structure **XII** corresponds to a minimum on the PES for $C_5H_4O_3$; here, the O···O contact is somewhat shorter [2.645 Å (MP2), 2.696 Å (B3LYP)] than the sum of the standard van der Waals

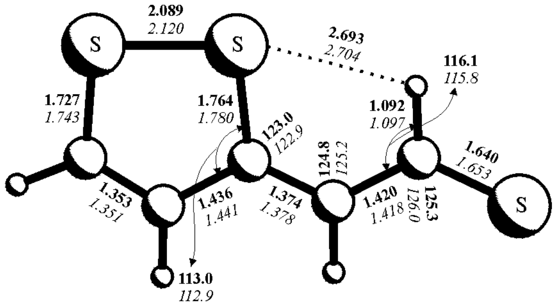
Table 2. Results of *ab initio* [(MP2(full)/6-31G**] and DFT (B3LYP/6-31G**) calculations of structures **IIIa**, **IIIb**, and **XII–XIV**

Structure no.	Method	λ	E_{tot}, a.u.	Δ*E*, kcal/mol	ZPE, a.u.	ΔE_{ZPE}, kcal/mol	Δ*H*, kcal/mol	ω, cm^{-1}
IIIa	MP2	0	–417.312025	9.1	0.082144	8.5	8.4	102
	B3LYP	1	–418.461888	7.8	0.080397	6.6	6.2	*i* 217
XII	MP2	0	–417.326465	0	0.083060	0	0	125
	B3LYP	0	–418.474259	0	0.082325	0	0	124
XIII	MP2	0	–417.326712	–0.2	0.082944	–0.3	–0.3	94
	B3LYP	0	–418.474734	–0.3	0.082225	–0.4	–0.3	100
IIIb	MP2	0	–1385.259195	0	0.077923	0	0	108
	B3LYP	0	–1387.493343	0	0.076047	0	0	159
XIV	MP2	0	–1385.239871	12.1	0.076621	11.3	11.3	47
	B3LYP	0	–1387.472697	13.0	0.075453	12.6	12.8	64

[a] See note [a] to Table 1.



IIIb, C_{2v}, $\lambda = 0$



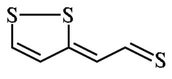
XIV, C_s, $\lambda = 0$

Fig. 6. Geometric parameters (bond lengths, Å, and bond angles, deg) of structures **IIIb** and **XIV**, calculated by the MP2(full)/6-31G** (boldface numbers) and B3LYP/6-31G** methods (italicized numbers). The experimental data were taken from [2].

radii of oxygen atoms (2.8 Å) [5]. The calculation of the corresponding *trans-s-trans*-structure **XIII** showed that isomers **XII** and **XIII** have similar energies, though the latter is by 0.2 (MP2) or 0.3 kcal/mol (B3LYP) more stable. This suggests a repulsive character of the O···O interaction. In going from *cis-s-cis*-**XII** to *trans-s-trans*-**XIII** the carbon–carbon bond lengths almost do not change; this means that the character of conjugation (aromaticity) also remains unchanged. The calculated geometry and energy parameters of structures **IIIa**, **XII**, and **XIII** are given in Fig. 5 and Table 2.

1,6,6a-Trithiapentalene structures. Unlike structure **IIIa**, planar bicyclic molecule **IIIb** has a C_{2v} symmetry and corresponds to a minimum on the PES. The S···S distance in **IIIb** is 2.367 Å (MP2) or 2.422 Å (B3LYP), i.e., it is considerably shorter than the sum of the standard van der Waals radii of sulfur atoms (3.7 Å) [4]; therefore, the S···S interaction in **IIIb** is attractive, and it leads to formation of a strong three-center four-electron S–S–S bond.

The energy of hypervalent S···S interaction in structure **IIIb**, which was estimated as the difference between the total energies of *cis-s-cis*- and *trans-s-trans*-isomers **IIIb** and **XIV**, is 12.1 (MP2) or 13.0 kcal/mol (B3LYP). In going from structure **IIIb** to **XIV**, the alternation of carbon–carbon bonds increases by about 0.05 Å, indicating a considerable contribution of aromatic stabilization of the bicyclic pentalene structure (**IIIb**). The calculated geometry and energy parameters of structures **IIIb** and **XIV** are given in Fig. 6 and Table 2. The calculated structural parameters of **IIIb** agree well with the experimental data reported in [2] and with the results of theoretical study of trithiapentalene [4].



XIV

REFERENCES

1. Minkin, V.I., *Ross. Khim. Zh.*, 1999, vol. 43, pp. 10–21.
2. Gleiter, R. and Gygax, R., *Topics in Current Chemistry*, Berlin: Springer, 1976, vol. 63, pp. 49–88.
3. Minyaev, R.M. and Minkin, V.I., *Can. J. Chem.*, 1998, vol. 76, pp. 81–89.
4. Takane, S. and Sakai, S., *J. Mol. Struct. (Theochem)*, 1999, vol. 488, pp. 1–10.
5. Emsley, J., *The Elements*, Oxford: Clarendon, 1989, Translated under the title *Elementy*, Moscow: Mir, 1993, p. 256.
6. Frish, M.J., Trucks, G.W., Schlegel, H.B., Gill, P.M.W., Johnson, B.G., Robb, M.A., Cheeseman, J.R., Keith, T.A., Petersson, G.A., Montgomery, J.A., Raghavachari, K., Al-Laham, M.A., Zakrzewski, V.G., Ortiz, J.V., Foresman, J.B., Peng, C.Y., Ayala, P.Y., Chen, W., Wong, M.W., Andres, J.L., Replogle, E.S., Gomperts, R., Martin, R.L., Fox, D.J., Binkley, J.S., Defrees, D.J., Baker, J., Stewart, J.P., Head-Gordon, M., Gonzalez, C., and Pople, J.A., *Gaussian-94. Revision B3*, Pittsburgh (PA): Gaussian, 1995.
7. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S.J., Windus, T.L., Dupuis, M., and Montgomery, J.A., GAMESS Version 25, March 2000, *J. Comput. Chem.*, 1993, vol. 14, pp. 1347–1363.
8. Minkin, V.I., Simkin, B.Ya., and Minyaev, R.M., *Quantum Chemistry of Organic Compounds. Mechanism of Reactions*, Berlin: Springer, 1990.
9. *PCMODEL*, Bloomigton (IN): Selena Software, 1987.

10. Shiött, B., Inversen, B.B., Madsen, G.K., and Bruice, T.C., *J. Am. Chem. Soc.*, 1998, vol. 120, pp. 12117–12124 (see also references therein for earlier studies).
11. Madsen, G.K., Inversen, B.B., Larsen, F.K., Kapon, M., Reisner, G.M., and Herbstein, F.H., *J. Am. Chem. Soc.*, 1998, vol. 120, pp. 10 040–10 045.
12. Winnewisser, G., Winnewisser, M., and Gorgy, W., *J. Chem. Phys.*, 1968, vol. 49, no. 8, pp. 3465–3478.
13. Stryer, L., *Biochemistry*, San Francisco: W.H. Freeman, 1981, 2nd ed. Translated under the title *Biokhimiya*, Moscow: Mir, 1984, vol. 1.
14. Curci, R. and Edwards, J.O., *Catalytic Oxidations with H_2O_2 as Oxidant*, Strucul, G., Ed., Dordrecht: Reidel–Kluwer, 1992, chap. 3.
15. Curci, R., *Advances in Oxygenated Processes*, Baumstark, A.L., Ed., Greenwich (CT): JAI, 1990, vol. 2, chap. 1, pp. 1–59.
16. Carey, F.A. and Sundberg, R.J., *Advances in Organic Chemistry*, New York: Plenum, 1990, part A, p. 284.