

AN IODABENZENE STORY

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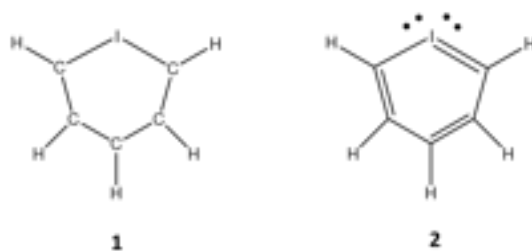
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ABSTRACT: We call iodabenzene a cyclic $(\text{CH})_5\text{I}$ molecule. A planar iodabenzene would have 8 π electrons, a situation best avoided by an out-of-plane distortion to a bird-like geometry. The electronic structure and charge distribution of this molecule resemble those of Meisenheimer complexes, derivatives of $(\text{CH})_5\text{CH}_2^-$. A similar substitution strategy, of π -acceptors in *ortho* and *para* positions, works in both cases to planarize and stabilize such derivatives. Some 40 kcal/mol (73 kcal/mol for the unsubstituted case) below the bird, a classical 5-iodocyclopentadiene structure awaits, reached through a bicyclic transition state. The calculated activation barrier for the highly exothermic reaction to a classical Lewis structure nevertheless make us optimistic about the chances of detecting, even isolating the bird isomer.

INTRODUCTION

Prompted by a question from Gerald F. Koser at Univ. of Akron, we began to think about iodabenzene, represented by the structure **1**. As drawn, this structure is not meant to carry any implication about the bonding in the molecule; it only indicates atom connectivity. Note, however, that this molecule, were it to be planar, would have two more electrons than a hypothetical $(\text{CH})_5\text{I}^{2+}$ ring, which would be iso-valence electronic with the well-known pyrylium ion $(\text{CH})_5\text{O}^+$ and pyridine, $(\text{CH})_5\text{N}$. Those two electrons in excess of an aromatic sextet are likely to enter a ring π -antibonding orbital, not a good thing. Writing a hypervalent structure^{1,2,3} (**2**) seems like a way out, but detailed consideration of the placement of electrons in such a molecule leads one back to an 8π system.



Iodabenzene and other “halogenabenzenes” were in fact, introduced in the literature by Glukhovtsev.⁴ He thought of two possibilities for halogenabenzene: If the two excess electrons provided by the halogen were to occupy a π level, we would have as mentioned, an 8π electron antiaromatic system. On the other hand, if they were to occupy a C-I-C antibonding σ -orbital, we might have a 6π -electron aromatic species. Glukhovtsev found that the former situation is preferred to the latter, and that the structure of the 8π electron system is planar, based on AM1 and MNDO

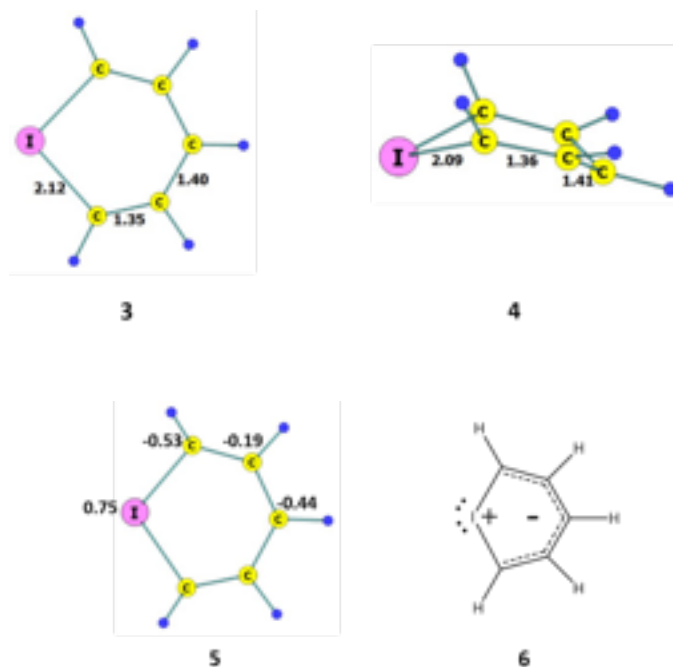
calculations. In this paper, we revisit the seemingly simple iodabenzene structure. It leads us to an informative exploration of alternative C₅H₅I structural possibilities.

RESULTS AND DISCUSSION

The calculations we report are both wave-function based and DFT ones, at the B3LYP, M06-2X and MP2 levels,⁵⁻⁶ with details given in the Supplementary Information (SI) to this paper. We used Def2-TZVPP basis set for all calculations.⁷ We also applied multireference calculations to accurately calculate the singlet-triplet gap.^{8,9} Unless otherwise stated, the calculational results shown are M06-2X type, which gives good main group thermochemistry and kinetics.¹⁰ The bond lengths are in Å, and energies are in kcal/mol, throughout the paper. The relative energy values include zero point corrections. The free energy values include thermal corrections corresponding to 298.15 K.

A C_{2v}-constrained optimization of **1** led to **3**. However, planar **3** was characterized by one imaginary frequency in its Hessian matrix; following that mode led to a non-planar, graceful bird-like structure shown in **4**, which is 6 kcal/mol lower in energy. We shall use this colloquial descriptor, bird, from this point on. The charges resulting from a natural population analysis¹¹ (there is some dependence on the method used) are shown in **5**. These are consistent with an iodonium ion bridging a pentadienyl anion, valence structure **6**. Note especially the accumulation of negative charge *ortho* and *para* to iodine. Iodonium salts are, of course, common polyvalent iodine compounds.¹² The planar system has eight π -type electrons; the non-planarity

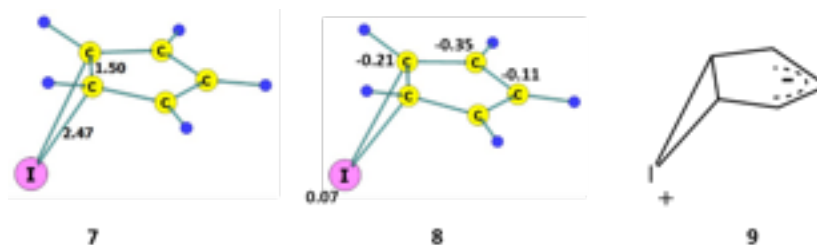
of the bird form is an attempt to escape from this situation, as we will see in a detailed orbital picture further on in this work.



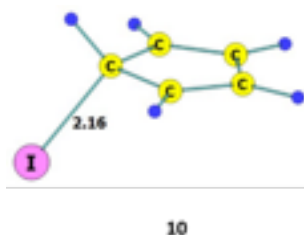
We note at this point that Glukhovtsev in his previous work also came up with the preferred zwitterionic valence structure for iodobenzene. Also, as we would infer from the charge distribution of **5** or **6**, the zwitterionic structure would be less likely as the electronegativity of the halogen increases. In fact, we found local minima for bird structures of $(\text{CH})_5\text{X}$, $\text{X} = \text{Br}, \text{Cl}$, but no local minimum of this geometry for $\text{X} = \text{F}$, at B3LYP and MP2 levels. Fluorobenzene is a shallow minimum at M06-2X level.

A Bicyclic Alternative. A structure related to **4** is the bicyclic one (**7**), which turns out to be not a local minimum, but a transition state. The charge distribution in **7** is shown in **8**. At first sight, one might think that with a fully formed CC bond, **7** might be described by valence structure **9**, the result of a formally an allowed disrotatory

six-electron electrocyclic reaction.¹³ However the positive charge on the I is much smaller than in the bird, and the C-I bonds in **7** are also very long. The charge distribution (**8**) also is not consistent with Lewis structure **9**. It is better to think of the bicyclic structure as a transition state for an allowed 1,5-(=1,2-) sigmatropic shift on a 5-iodocyclopentadiene; we will return to this perspective.



And Classical Structures. The bicyclic structure **7**, though 55 kcal/mol more stable than the bird, has, however, one imaginary frequency. Following the vector indicated by the vibration, we are led to the still more stable 5-iodocyclopenta-1,3-diene,¹⁴ **10**, which is no less than 73 kcal/mol lower in energy than the bird structure (**4**). Given that the birds are computed to be local minima, and the bicyclic structures are not, we wondered what kind of barrier protects the bird structures from highly exothermic decomposition to the classical substituted cyclopentadienes.



The mechanism of isomerization was explored by a potential energy surface scan and is summarized in Fig. 1. The reaction **4** → **10** has a barrier of 14 kcal/mol,

through transition state **11**, which retains the C_s symmetry of the bird. The path to product continues with a mirror plane of symmetry maintained until effectively a bicyclic structure (**7**) is reached, at which point the reaction bifurcates along two enantiomeric paths leading to a cyclopentadienyl iodide structure (**10**). Such “two-step-no-intermediate” mechanisms are known for a number of potential energy surfaces.¹⁵ Structure **7** may also be viewed as the already studied 1, 2-halogen-migration transition state of cyclopentadienyl halides.¹⁶⁻¹⁷ The activation barrier for 1,2-iodine migration calculated for **10** in ref. 17 (≈ 20 kcal/mol) at MP2/6-31+g(d) is close to that calculated by us (19 kcal/mol). The geometries are also close to each other.

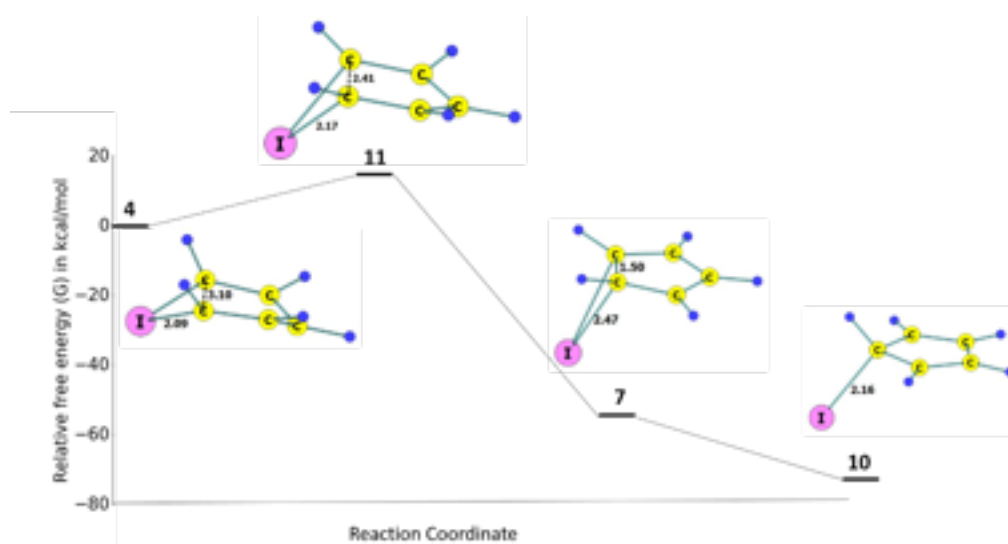


Figure 1. Mechanism of isomerization of iodabenzene.

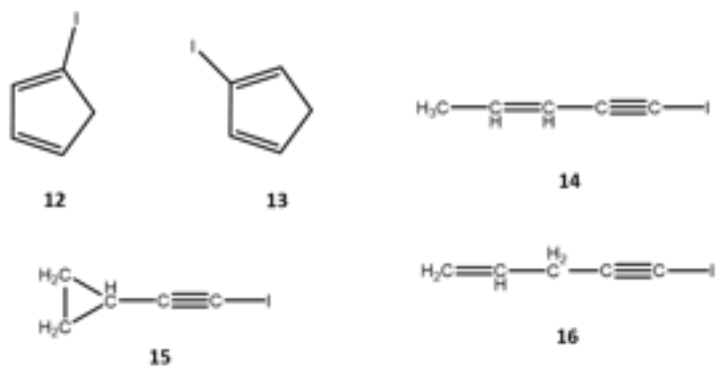
The relative energies of the bird and cyclopentadienyl structures of ioda-, bromo-, chlora- and fluorabenzenes and the barrier for bird to cyclopentadienyl isomerization are shown in Table 1, as are the natural charges on the halogen atom in

the bird structures. The higher relative energy and low activation barrier of fluorobenzene is consistent with the zwitterionic nature of the molecule.

Table 1. Comparison of iodobenzene to the Br, Cl, and F analogs.

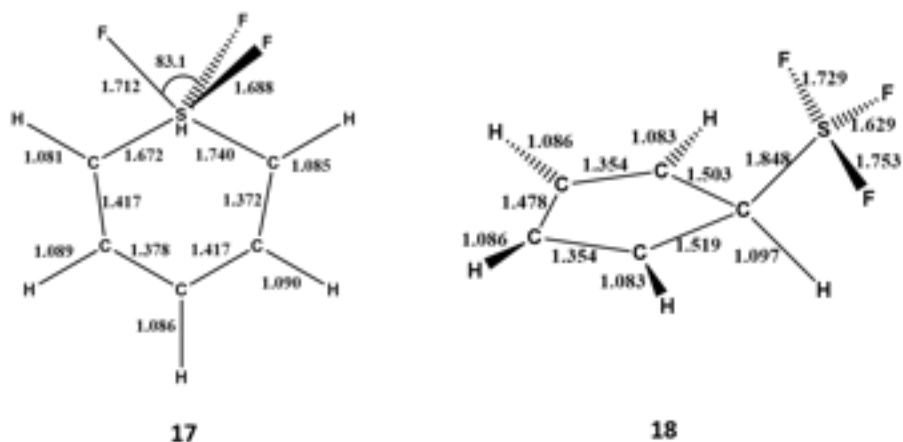
| X in C ₅ H ₅ X | Energy of the bird structure relative to the 5-halo-cyclopentadiene, in kcal/mol | Barrier (ΔG^\ddagger) for the isomerization from bird to 5-halocyclopentadiene (kcal/mol) | Charge on X in the bird structure |
|--------------------------------------|--|---|-----------------------------------|
| I | 73 | 14 | 0.75 |
| Br | 73 | 13 | 0.59 |
| Cl | 72 | 13 | 0.49 |
| F | 92 | 2 | -0.18 |

Of course, the 5-iodocyclopentadiene structure (**10**) does not exhaust the isomeric possibilities for stoichiometry C₅H₅I. 1- and 2-iodocyclopentadiene structures **12** and **13** come to mind, as do the isomers of **14-16** and still other constitutional isomers. We have not explored in detail the variety of available Lewis structures, as we wanted to remain close to the monocyclic form. However, all the iodocyclopentadiene isomers are close to each other in energy, while **14-16** lie 30-40 kcal/mol higher.



We note that Glukhovtsev, Laiter and Simkin, in a study of halogenacyclobutadienes, $(\text{CH})_3\text{X}$ (now with an aromatic π -electron system) also found that classical isomers were much stabilized.¹⁸

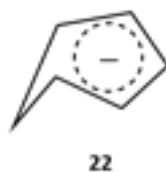
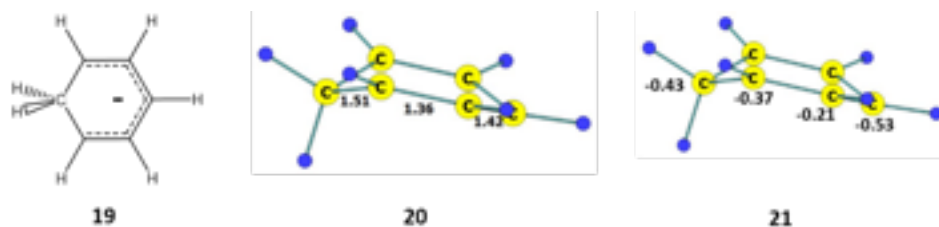
An SF_3 Analogue. There is an intriguing study by Xie, Schaefer, and Thrasher of an SF_3 analogue of the iodabenzene.¹⁹ The equilibrium structure they obtained is shown in 17.



Seeing a resemblance between the flat iodabenzene ring geometry and 17, we told our story to H. F. Schaefer. Y. Xie then proceeded to study structural alternatives analogous to our bicyclic (7) and cyclopentadienyl (10) isomers. The Georgia group indeed located these,²⁰ approximately 5 and 37 kcal/mol more stable than 17. We

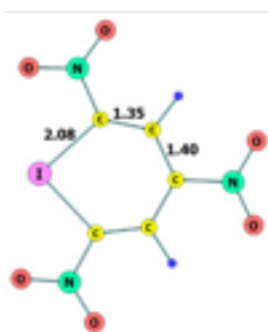
show the lowest energy structure they obtained, **18**. It may be seen as an SF₃-substituted cyclopentadiene, or alternatively as a hypervalent SF₄ with one F substituted by a cyclopentadienyl group.

An Analogy Between Iodobenzene and a Meisenheimer Complex. The pentadienyl anion moiety in **6** immediately calls up an analogy to the known Meisenheimer complexes **19**.^{21,22} Optimization of the parent structure of these, C₆H₇⁻ (**19**), gave structure **20**, which indeed shows a remarkable geometrical similarity to the bird iodobenzene (**4**). The charge distribution of **20**, shown in **21**, indicates that the *ortho* and *para* positions are more negatively charged than the *meta* position, similar to iodobenzene bird.

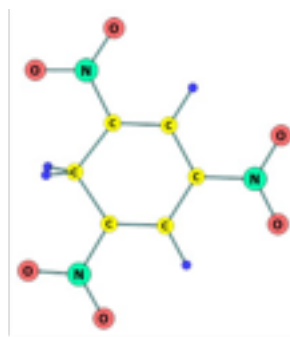


Recent computational studies on $C_6H_7^-$ also find the bird-like geometry.²³ Earlier theoretical investigations by Olah and Haddon report a planar C_{2v} structure for $C_6H_7^-$ at the MINDO/3 level.^{24,25} Haddon also located a second local minimum at higher energy, corresponding to what he called a homocyclopentadienide ion, **22**. This is like the bicyclic geometry that we explored above for iodabenzene. Homoconjugation was very much in the air at the time, and $C_6H_7^-$ was the subject of some discussion and good experiment.^{26,27,28}

How to stabilize iodabenzene? We are not deterred by the 73 kcal/mol instability of the bird form. The similarity in geometry, electronic structure and charge distribution immediately suggests a strategy of stabilizing the iodabenzene structure, analogous to that used in the Meisenheimer complexes: Put π -acceptors in the *ortho* and *para* positions.²⁸ We examined iodabenzene, substituted in *ortho* and *para* positions with nitro groups (**23**), where the negative charge accumulates. Similar to the trinitro-substituted Meisenheimer complex (**24**), trinitro-iodabenzene (**23**) is calculated as planar. We also examined the corresponding Br, Cl and F analogs. While trinitro-bromobenzene is computed as a planar minimum, the Cl and F analogs are calculated as minima with bird structure.



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Table 2. Effect of π -accepting substituents on the stability of halogenabenzenes.

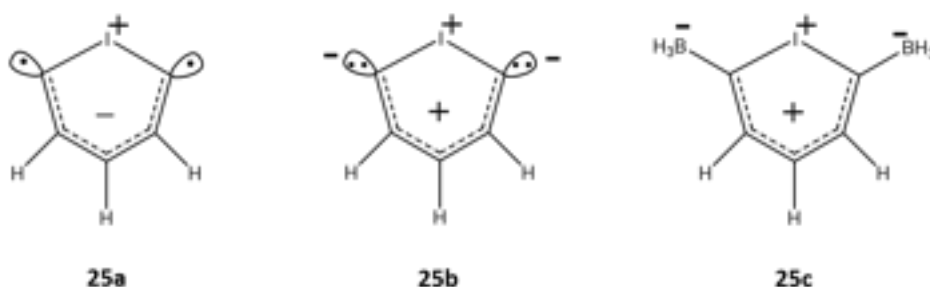
The natural charge on halogen atom is also shown. The zero of energy is the 5-cyclopentadienyl halide in each case.

| Halogen in halogenabenzene | Substituent (<i>ortho</i> , <i>para</i> -trisubstitution) | Relative energy in kcal/mol | | Barrier for the isomerization from bird or planar to cyclopentadienyl (kcal/mol). | Charge on X in the bird or planar structure |
|----------------------------|--|-----------------------------|--------|---|---|
| | | bird | planar | | |
| I | -NO ₂ | ---- | 40 | 30 | 1.06 |
| | -CN | 55 | ---- | 18 | 0.90 |
| Br | -NO ₂ | ---- | 49 | 23 | 0.79 |
| | -CN | 57 | ---- | 16 | 0.70 |
| Cl | -NO ₂ | 54 | ---- | 19 | 0.63 |
| | -CN | 57 | ---- | 16 | 0.58 |
| F | -NO ₂ | 83 | ---- | 6 | -0.11 |
| | -CN | 78 | ---- | 7 | -0.14 |

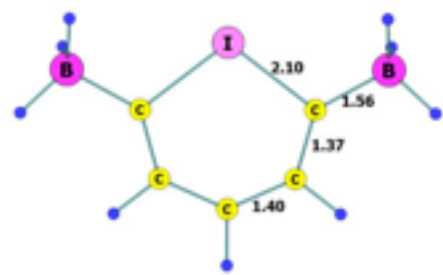
We also tried some structures with -CN groups as substituents in *ortho* and *para* positions; these are also local minima with the bird structure for all halogens. Table 2 lists the energy values of the nitro- and cyano- substituted halogenabenzenes relative to the 5-cyclopentadienyl structure, and the barrier for their isomerization. Note the general stabilization of the planar or bird compounds by 10-30 kcal/mol (relative to the unsubstituted case) on trinitro or tricyano substitutions. At the same time, the barrier for the isomerization from the halogenabenzene to cyclopentadienyl increases

with substitution by π -accepting groups. The increase in the positive charge on halogen accompanying π -accepting substitution is also evident from a comparison of Table 1 and 2. Planarization can be achieved even with a single NO_2 substituent, provided it is in the *ortho* position where the negative charge is maximum. We think the trinitro and tricyano bird halogenabenzenes (not F) may be isolable compounds at low temperatures.

Another strategy to remove two electrons from the π -system of iodabenzene comes to mind. Imagine the following sequence of hypothetical reactions: (a) Remove the *ortho* hydrogens from iodabenzene. That leaves a diradical **25a**. (b) Take the two “extra” electrons from the eight-electron π -system of **25a**, and put them into the σ -system, **25b**. (c) Add two boranes, BH_3 , to stabilize the new σ -electron pairs, reaching a zwitterionic valence structure **25c**.

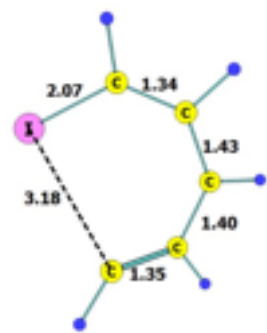


Structure **25c** was computed to be a planar 6π -electron aromatic system (**26**). Replacement of BH_3 with isolobal transition metal fragments should also be feasible. Once again, the less likely F analog is not a minimum. The natural charge on iodine in **26** is 0.96 compared to 0.75 in **4**.



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A triplet state for the bird. The bird structure 4, attractive as it is, is of high energy and the HOMO-LUMO gap is 5.5 eV. For high energy singlet structures, one needs to think about the possibility of low lying triplet states. We indeed found a triplet state, **27**, which is only 4 kcal/mol higher in energy. This is an unrestricted M06-2X result, and we were worried if this method was adequate for estimating the singlet-triplet splitting. So, we also carried out GMC-QDPT calculations^{29,30} with an active space of 10 orbitals and 12 electrons and obtained results qualitatively consistent. The triplet state is 5.5 kcal/mol higher in energy than the singlet at GMC-QDPT level. In the triplet state, one unpaired electron occupies the π^* level and the other enter a C-I antibonding σ^* level. A symmetry lowering induced by what could be viewed as a pseudo-Jahn-Teller effect concentrates the C-I antibonding interaction on one side, resulting in an elongated I-C bond. An unsymmetric distortion ensues.



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Structure and bonding. The bird structure of iodabenzene is related to the boat structure of benzene dianion, $C_6H_6^{2-}$.³¹⁻³² The two excess electrons in $C_6H_6^{2-}$ occupy LUMO1 of benzene (Fig. 2) and the structure would be expected to pucker to decrease the antibonding interaction between neighboring atoms and also (perhaps) to turn on a cross-ring overlap, as shown by the dotted line. Indeed, normally the puckered structure is preferred to the planar one, unless the out-of-plane distortion is sterically prevented.³⁷ Examples of both puckered and undistorted structures are known in literature, where the H of $C_6H_6^{2-}$ are replaced by silyl groups.³⁷

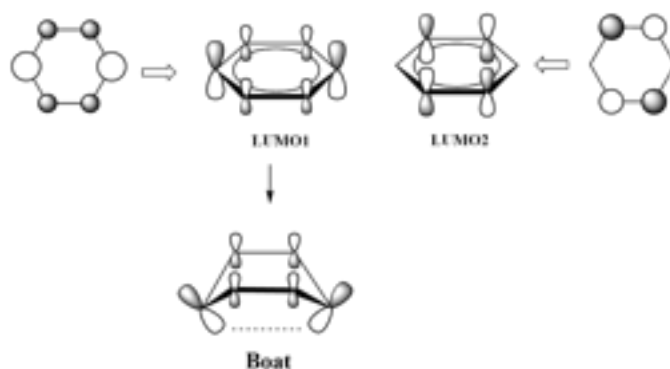


Figure 2. LUMOs of benzene and the transformation of LUMO1 in the boat structure

We think that the reason for puckering of iodabenzene is similar. The HOMO in planar and bird structures is shown in two views in Fig. 3. Notice how the puckering helps in decreasing the antibonding interaction between I and C in the HOMO. The HOMO of $(CH)_5I$ gets stabilized by 0.7 eV on puckering.

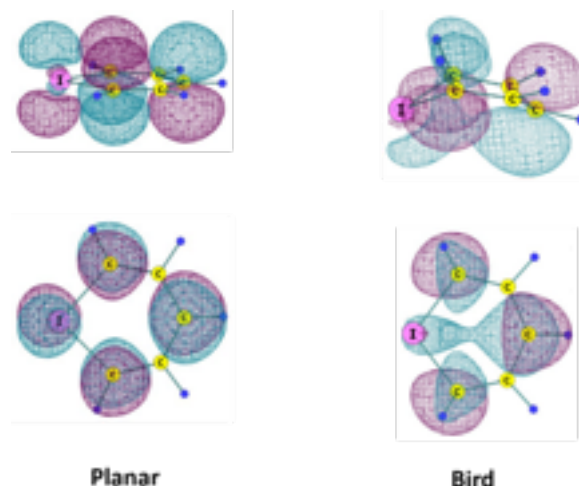
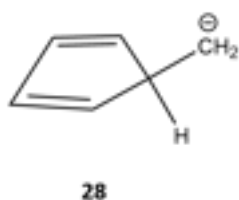


Figure 3. HOMO of iodobenzene planar and bird structures, shown in two views.

The analogy we found between the Meisenheimer complex and bird iodobenzene has limitations. So the cyclopentadienyl structure of the Meisenheimer complex (**28**) is less stable than the bird structure (**20**) by 35 kcal/mol. This is understandable, as structure **28** leads to localization of negative charge on the primary carbon atom.



CONCLUSION

Iodobenzene, formally an antiaromatic 8π -electron system, acquires stability by an out-of-plane puckering, which decreases the antibonding interaction in the HOMO. The resulting bird structure is similar in charge distribution and geometry to the well-known Meisenheimer complex. The resemblance leads to the same strategy as one would use to stabilize the Meisenheimer complex for iodobenzene, i.e., to put π -

accepting substituents in the *ortho* and *para* positions, where the negative charge accumulates. Way downhill in energy, a classically bonded iodocyclopentadiene structure awaits (CH)₅I. While the barrier for the isomerization from iodabenzene bird to the cyclopentadienyl structure is calculated as only 14 kcal/mol, that for the trinitro-substituted one is 30 kcal/mol. This makes us optimistic about the experimental realization of the bird iodabenzene isomer.

ASSOCIATED CONTENT

Supporting Information

Coordinates and energies of the computed structures.

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Author Contributions

AMR designed, carried out and interpreted research, wrote paper; PCP designed, carried out and interpreted research, wrote paper; TZ contributed calculations and methodology; RH designed and interpreted research, wrote paper.

Notes

The authors declare no competing financial interest.

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