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Benzene triradicals: stabilization or destabilization?

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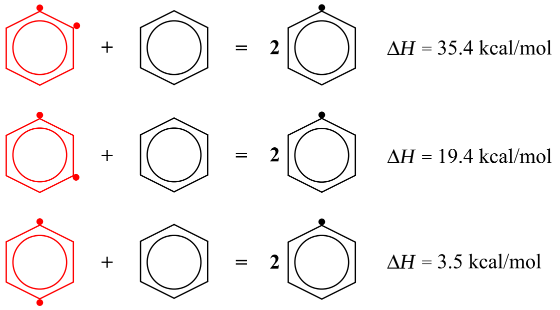
ABSTRACT

A new group additivity scheme has been developed to evaluate the stabilization/destabilization effects of benzene triradicals. It is shown that benzene triradicals manifest a significant destabilization effect and not stabilization effect as previously thought.

Recently there has been an increasing interest in the electronic structure and stability of benzene polyradicals as well as of related heterocompounds.[1–5] Apart from their close involvement in many chemical processes such as decomposition and combustion[6] as well as their potential applications in building organic magnets[7] these species represent remarkable models for developing and refining new computational and interpretational tools. The benzene triradicals have been subject to extensive thermochemical and spectroscopic studies. Thus, Wenthold and co-workers[1] experimentally determined the heat of formation and bond dissociation energies of 1,3,5-tridehydrobenzene while Sander and co-workers isolated and spectroscopically characterized 1,2,3-tridehydrobenzene.[8] In this respect, one of the most interesting problems is the evaluation and rationalization of the stabilization/destabilization energies in benzene polyradicals. When it comes to diradicals the problem is straightforward in that we are limited by the choice of reference species (benzene and phenyl radical) and, hence, the reaction scheme used to evaluate the stabilization/destabilization energies is unique. Thus, the diradical stabilization energy (DSE) is defined as the enthalpy change of the following reactions.[9]

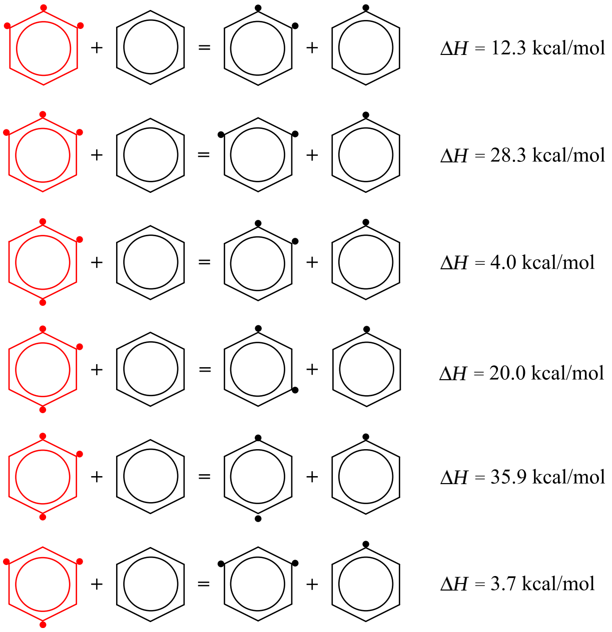


ΔH = 35.4 kcal/mol

ΔH = 19.4 kcal/mol

ΔH = 3.5 kcal/mol

The positive sign of the DSE indicates that there is a *net stabilization* of the diradicals with respect to monoradicals. For triradicals, however, the situation is not as trivial in that the number of reference species is higher and, therefore, there exist multiple options in defining and evaluating the stabilization/destabilization effects. A natural extension of the reasoning employed in the definition of the DSE is to evaluate the triradical stabilization energy (TSE) as the enthalpy changes of the following reactions.[1–3]



ΔH = 12.3 kcal/mol

ΔH = 28.3 kcal/mol

ΔH = 4.0 kcal/mol

ΔH = 20.0 kcal/mol

ΔH = 35.9 kcal/mol

ΔH = 3.7 kcal/mol

There are several problems with this definition, however. First, these reaction schemes predict a *net stabilization effect* for triradicals which is difficult to rationalize. Indeed, from general physicochemical principles one would expect an opposite effect, that is, a *destabilizing effect* in triradicals when compared to biradicals. Second, the above reaction schemes are not unique. Other reaction schemes may be envisioned such as those presented in the next figure which clearly show a net destabilizing effect! Finally, and most importantly, the above reaction schemes defining the TSE

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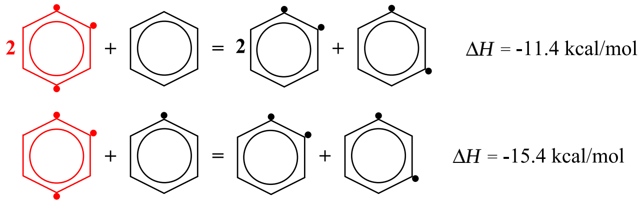
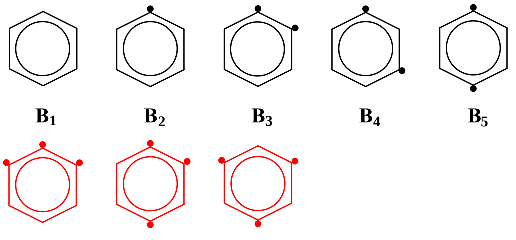


as well as the reactions describing stepwise formation of mono-, bi-, and triradicals from benzene (bond dissociation energies) do not properly balance the number and type of interactions among radicals. Moreover, since the absolute energy increments of various types of interactions among radical centers are not available the only way to accurately determine the stabilization/destabilization effects is to design reaction schemes that maximally balance the number and type of interactions. The purpose of this Letter is to perform an accurate evaluation of the stabilization/destabilization effects in benzene triradicals.

As well known, there are two main approaches to the evaluation of various types of stabilization/destabilization effects such as aromatic stabilization energies, strain energies, conjugation, and hyperconjugation.[10] One of them is based on the group additivity schemes.[11] According to the group additivity approach, the stabilization/destabilization effects in a certain species are evaluated as the difference between the enthalpy of formation calculated via a group additivity scheme and its experimental enthalpy of formation. The other method employs a single reaction scheme that balances the number and type of groups or interactions in species involved in the reaction scheme. For instance, balancing the number and type of bonds in the reaction scheme results in the so-called isodesmic stabilization/destabilization energies.[12] We have recently shown that these two methods are essentially identical in that the group additivity methods can be partitioned into a sum of contributions associated with reaction schemes that preserve the type and number of groups or interactions.[13] The only difference between the group additivity and single reaction scheme approaches is in the number of reference species. Usually, the group additivity schemes are developed employing a large number of reference species. This is tantamount to a large number of possible reaction schemes. A good group additivity scheme should, in general, result in the same stabilization/destabilization energy for any conceivable reaction scheme. In reality, there are slight differences that are normally overcome by a rigorous statistical averaging over all reaction schemes. On the other hand, a single reaction scheme approach employs a limited number of reference species from the full list of species that are used in the group additivity method, for example, a minimal number of species necessary to write a reaction that completely balance the number of groups and interactions. Provided the reference species are carefully selected, the differences between group additivity and single reaction schemes are small.

In the case of benzene triradicals the list of reference species is limited to the first five species B_1, B_2, B_3, B_4, and B_5 in the following list:



B_1 **B_2** **B_3** **B_4** **B_5**

B_6 **B_7** **B_8**

We are interested in evaluating the stabilization/destabilization energies of the benzene triradicals, that is, the last three species B_6, B_7, and B_8. Due to the structural particularity of the reference species, that is, the number and position of the radicals, we are also limited in the selection of groups or interactions. It is natural to accept as 'groups' the pair interactions between hydrogen and radical centers. There are three different types of such interactions, namely, H–H, H–**.** and **.**–**.** interactions. In turn, each of these types of interactions may be located in *ortho*, *para*, and *meta* positions, thus, resulting into a total of nine groups. The respective group matrix is presented in Table 1. An elementary linear algebra analysis (details may be found in the Supplementary data) shows that the rank of the group matrix is equal to five. In other words, only five groups from a total of nine are linearly independent. Since we have only five reference species it also means that the number of groups we have selected (nine) is maximal in the sense that extending the number of groups to higher order interactions would make the analysis unworkable. Rather than assigning arbitrary and, hence, meaningless values to the group values we prefer to equivalently generate reactions involving each triradical and reference species that balance all types and numbers of groups. Because the rank of the group matrix is equal to five and a reaction should involve at least six species there is only one such reaction for each triradical. It may be shown that the enthalpy changes of these, so-called group additivity, reactions are precisely equal to the differences between the enthalpies of formation evaluated via the group additivity scheme and the experimental enthalpies of formation of triradicals, that is, represent the stabilization/destabilization energies. The respective group additivity reactions and their enthalpy changes are

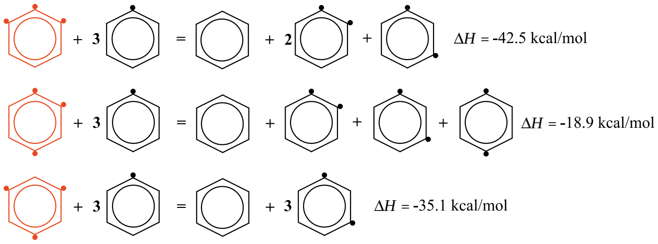


Table 1
Group additivity matrix for benzene radicals

	o-HH	*m*-HH	*p*-HH	*o*-H·	*m*-H·	*p*-H·	*o*-¨	*m*-¨	*p*-¨	$\Delta_f H_i^{0a}$ (kcal/mol)
B_1	6	6	6	0	0	0	0	0	0	19.7
B_2	4	4	4	2	2	2	0	0	0	80.5
B_3	3	2	2	2	4	4	1	0	0	105.9
B_4	2	3	2	4	2	4	0	1	0	121.9
B_5	2	2	4	4	4	0	0	0	2	137.8
B_6	2	1	0	2	4	6	2	1	0	154.4
B_7	1	1	2	4	4	2	1	1	2	162.7
B_8	0	3	0	6	0	6	0	3	0	179.0

o-HH, *m*-HH, *p*-HH—interaction between hydrogen atoms in *ortho*, *meta*, and *para* positions.
o-H·, *m*-H·, *p*-H·—interaction between hydrogen atoms and radical centers in *ortho*, *meta*, and *para* positions.
o-¨ *m*-¨ *p*-¨—interaction between radical centers in *ortho*, *meta*, and *para* positions.
[a] Data from Refs. 1 and 2.

As can be seen, all of the triradicals show *a significant destabilization effect* with respect to reference species. The experimental enthalpy changes of these reactions are reasonably close to those predicted by computational methods. Thus, the enthalpy changes of these reactions at 0 K calculated using low-spin SF-CCSD (ROHF) gaps for the triradicals and diradicals[3] are −45.2, −17.5, and −30.6 kcal/mol, respectively.

In conclusion, the stabilization/destabilization effects in chemical species significantly depend on the selection of reference species and group additivity schemes. Once these are selected it is necessary to ensure that the reaction schemes properly balance the type and number of groups. The conventional definition of TSE is based on reaction schemes that neither define nor balance the groups or interactions. As a result, the conventional TSE is arbitrary. A rigorous analysis of the problem in terms of well-defined group additivity schemes reveals that triradicals manifest a destabilizing effect and not stabilizing effect as previously thought.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.086.

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