Magnetic susceptibility and aromaticity in the excited states of benzene

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A numerical method for obtaining the change in energy due to a magnetic field of given strength is applied to calculations of π-electronic delocalisation susceptibilities of the low-lying excited states of benzene. It is found that the delocalisation susceptibilities of the excited states of benzene are quite different from those of the ground state. On the basis of the calculated results, the aromaticity of the excited states of benzene is discussed.

The London susceptibility,[1] or the magnetic delocalisation susceptibility[2] is one of the important quantities of magnetic properties. Recently, a review article[3] on aromaticity and magnetic delocalisation susceptibilities has been published. The delocalisation susceptibility serves as an index of aromaticity, namely, one of the magnetic criteria of aromaticity.[4,5] However, the magnetic susceptibilities of the excited states and their aromaticity have not been examined. This paper deals with the magnetic susceptibilities and aromaticity of the low-lying excited states of benzene.

We examined the delocalisation susceptibilities of the excited states of benzene by using the Pariser–Parr–Pople-type SCF MO method with the variable bond–length technique[6] and the gauge-invariant atomic orbitals together with the parameterisation of Mikami, Miyai and Nakajima.[2] This method is quite simple, but for the ground-state susceptibilities, it yields quantitative results that are in agreement with the experimental values.[2] To obtain the excited states, the configuration interaction method was used, all single excitations being taken into account. We limited ourselves to the Frank–Condon excited states. Only the contribution from the orbital components of the magnetic susceptibility was considered and no contribution from the spin was included. Here, a numerical method for calculating π-electron (that is, delocalisation) susceptibility (K_π) was used.[7,8] The π-electron energy behaves as $\delta E = E(H) - E(0) = -(1/2)K_\pi H^2$ for small magnetic-field H. Therefore, K_π is obtained by evaluating $-2\delta E/H^2$ for very small values of H. The method was tested on the ground state of benzene with satisfactory results. The calculated value of the ground state of benzene ($K_{\pi b}(S0)$) is similar to that obtained by Davies[7] (-29.77×10^6 emu cm^3/mol).

The results are summarised in Table 1. The calculated magnetic susceptibilities are given in units of the magnetic susceptibility of the ground state of benzene ($K_{\pi b}(S0)$). In Table 1, therefore, positive values indicate diamagnetism whereas the negative values indicate paramagnetism.

Table 1 shows that the first excited singlet state (S1) that belongs to B_{2u} is calculated to be of large paramagnetism, its absolute value being about five times larger than that of the ground state, $K_{\pi b}(S0)$. In contrast, the calculated magnetic susceptibility of the second excited singlet state (S2) belonging to B_{1u} indicates substantial diamagnetism and its magnitude is about six times larger than $K_{\pi b}(S0)$. The third excited singlet state (S3), which is of E_{1u} symmetry, exhibits diamagnetism smaller than that of the ground state.

Table 1 also shows that the first excited triplet state (T1, $^3B_{1u}$) has paramagnetism, its absolute value being double than that of the ground state, $K_{\pi b}(S0)$. The second excited triplet state (T2, $^3E_{1u}$) and the third excited triplet state (T3, $^3B_{2u}$) are predicted to indicate diamagnetism: The calculated

Table 1   Calculated magnetic-susceptibilities ($K\pi$)

State	Symmetry	$K\pi/K\pi_b(S0)$
S1	B_{2u}	−4.79
S2	B_{1u}	6.29
S3	E_{1u}	0.75
T1	B_{1u}	−2.00
T2	E_{1u}	0.75
T3	B_{2u}	3.39

magnitude is 0.75 $K_{\pi b}(S0)$ for the $^3E_{1u}$ state and 3.4 $K_{\pi b}(S0)$ for the $^3B_{2u}$ state.

Comparison of the calculated magnetic-susceptibilities of the excited singlet and the corresponding excited triplet states, which have the same symmetry, shows that the $^1B_{2u}(S1)$ and the $^3B_{2u}(T3)$ states differ in the magnetic susceptibility from each other: the former state is markedly paramagnetic whereas the latter state is considerably diamagnetic. Similarly, the calculated susceptibilities of the $^1B_{1u}(S2)$ and the $^3B_{1u}(T1)$ states are quite different, the singlet state showing diamagnetism and the triplet state showing paramagnetism. In contrast, both the $^1E_{1u}(S3)$ and the $^3E_{1u}(T2)$ states have diamagnetism of the same magnitude.

On the basis of the calculated magnetic susceptibilities of the excited states, we discuss the aromaticity of the excited states from the viewpoint of the magnetic criteria of aromaticity. As shown in Table 1, the first excited singlet state $^1B_{2u}(S1)$ exhibits a large paramagnetism. This excited state is therefore predicted to be markedly antiaromatic. Since the magnetic susceptibility of the second excited singlet state $^1B_{1u}(S2)$ indicates it to be strongly diamagnetic, the $^1B_{1u}$ state is expected to have large aromaticity. The $^1E_{1u}(S3)$ state has a diamagnetic susceptibility that is 0.75 times larger than the ground state, and is hence predicted to be aromatic. Table 1 also predicts that the $^3B_{1u}(T1)$ state has antiaromaticity because this triplet state exhibits large paramagnetism (−2.00 $K_{\pi b}(S0)$). On the other hand, the $^3E_{1u}(T2)$ state is predicted to be aromatic. Further, the $^3B_{2u}(T3)$ state is expected to show substantial aromatic-character because of large diamagnetism (3.39 $K_{\pi b}(S0)$).

In conclusion, we have calculated the magnetic susceptibilities of the excited singlet and triplet states of benzene. It has been found that the magnetic susceptibilities of the excited states of benzene are different from that of the ground state. The nondegenerate excited states ($^1B_{2u}$, $^1B_{1u}$, $^3B_{1u}$, and $^3B_{2u}$) have been calculated to have large diamagnetism or large paramagnetism. The degenerate excited states ($^1E_{1u}$ and $^3E_{1u}$) have been expected to have diamagnetism smaller than the ground state. On the basis of the results, the aromaticity of the excited states has been discussed. The nondegenerate excited states have been predicted to show marked aromaticity or strong antiaromaticity whereas the degenerate excited states have been predicted to show aromaticity similar to the ground state.

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