

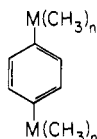
Anion States of Para-Disubstituted Benzenes: 1,4-Dihalobenzenes

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Abstract: The energies of the low-lying negative ion states of the 1,4-dihalobenzenes have been obtained by electron-transmission spectroscopy and compared with the results of SCF-MO calculations. Negative ion states associated with electron capture into benzene π^* orbitals as well as carbon-halogen σ^* orbitals are identified. The trends in the negative ion state energies can be explained on the basis of the inductive effect of the halogen substituents as well as the resonance interaction between substituent p-type lone pairs and benzene π orbitals.

For decades observation of the effect of chemical substitution in benzene has provided a basis for models describing substituent effects upon ultraviolet spectra, photoelectron spectra, and chemical reactivity of organic molecules.¹ Such models inevitably employ the molecular orbital (MO) picture of electronic structure and describe substituent effects in terms of the perturbation of orbitals localized on benzene by orbitals residing primarily upon the substituent. Attention is generally focused upon the outer-most occupied MO's and the innermost unoccupied MO's. For simplicity it is usually considered possible to treat σ and π orbitals separately and to separate the effect of substituents into the resonance and inductive contributions. In the spirit of this approach we have been studying para-disubstituted benzenes of the type



Beginning with group 4 substituents ($M = \text{C, Si, Ge, Sn; } n = 3$),² we have proceeded through groups 5 and 6³ and here present our results for the group 7 compounds—the 1,4-dihalobenzenes ($M = \text{F, Cl, Br; } n = 0$). It is the intent of this research that the nature of the substituent perturbation will provide insight into the bonding of these substituents with metal centers. In this work we employ electron-transmission spectroscopy (ETS) to measure the electron affinities associated with temporary anion formation arising from electron capture into low-lying unfilled orbitals. From these measurements, substituent effects upon the benzene π^* orbital energies can be inferred. For the group 4, 5, and 6 compounds our observations are interpretable in terms of simple perturbation theory arguments involving pseudo- π interactions between substituent σ^* orbitals and benzene π^* orbitals. There is also evidence for interaction with lone-pair orbitals on the atom (M) bonded to the benzene carbon. In the present case, however, since the dihalobenzenes are planar, there is no possibility of interaction between σ and π systems. The overriding interaction stems from the inductive effect of the very electronegative substituents. There is also evidence of a resonance interaction between substituent np-type lone pairs and the benzene π orbitals.

Experimental Section

Electron-transmission spectroscopy (ETS)⁴ is the conjugate to photoelectron spectroscopy (PES). Whereas PES measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of the negative ion state arising from electron capture into an unoccupied orbital. The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an inverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross

section only over a narrow energy range. Since the negative ion promptly decays by giving up the trapped electron, the formation and decay process appears as a sharp fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs. electron-energy spectrum, is referred to as a "resonance".

The electron spectrometer consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector.⁵ In practice the first derivative of the transmitted current as a function of energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance.⁶ The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum which characterizes the resonance.⁷ For the present purposes an attachment energy may be identified with the negative of the corresponding electron affinity (EA).⁷ The chief limitation is that ETS gives only the energy associated with unstable negative ions. That is, only negative electron affinities can be obtained with ETS.

Results

The derivative electron-transmission spectra of the 1,4-dihalogen benzenes along with the spectrum of benzene are presented in Figure 1. There are two features in the benzene spectrum; the first corresponding to electron capture into the degenerate pair of orbitals $\pi_4^*, \pi_5^*(e_{2u})$, and a second feature at higher energy corresponding to electron capture into $\pi_6^*(b_{2g})$.⁸ The first resonant state is sufficiently long-lived for vibrational structure to appear corresponding to the symmetric ring-breathing mode. Substitution in benzene lifts the (π_4^*, π_5^*) degeneracy. This is most evident in the spectrum of 1,4-difluorobenzene where two low-energy resonances appear in addition to the π_6^* resonance near 4.5 eV. In 1,4-dichlorobenzene and 1,4-dibromobenzene the (π_4^*, π_5^*) splitting is apparently so small as to be unobservable. In these compounds, however, a third feature appears at an energy intermediate between the (π_4^*, π_5^*) resonance and π_6^* resonance. The attachment energies (AE) measured from the ETS spectra

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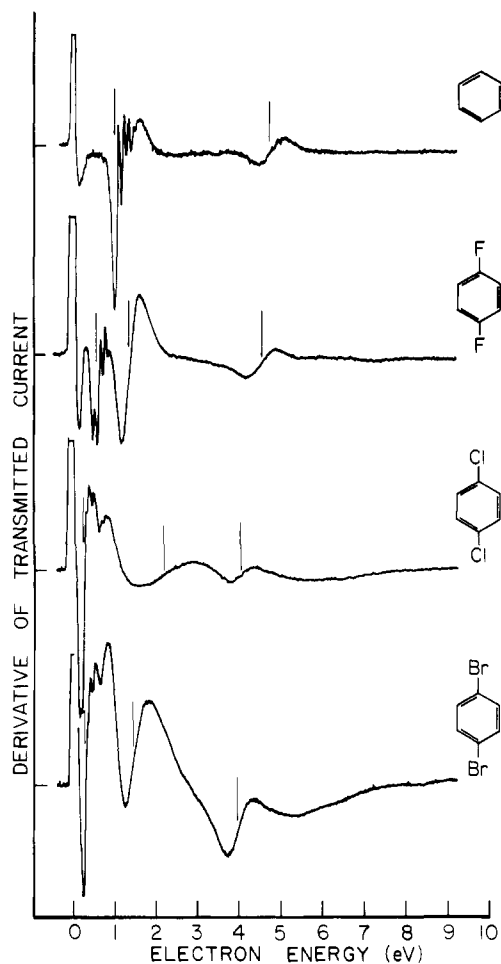


Figure 1. Derivative electron-transmission spectra of benzene and the para-dihalogen benzenes.

Table I. SCF-MO Orbital Energies (eV) for Benzene and Dihalobenzenes (The Symmetry of π_4^* and π_5^* Is Indicated)

	C_6H_6	$C_6H_4F_2$	$C_6H_4Cl_2$	$C_6H_4Br_2$
π_6^*	13.7	13.2	12.3	12.7
σ^*	15.8	14.4	9.2, 9.4	8.6, 8.7
π_5^*	7.3	7.1 (S)	6.1 (A)	6.4 (A)
π_4^*	7.3	6.7 (A)	5.8 (S)	6.3 (S)
π_3	-7.6	-7.1	-8.1	-7.3
π_2	-7.6	-8.2	-8.8	-8.5
π_1	-12.4	-11.6	-14.4	-13.7

along with vertical ionization potentials (IP) from photoelectron spectra⁹ are assembled in Figure 2 as a correlation diagram.

At the beginning of each electron-transmission spectrum there is a sharp positive spike followed by a negative dip. The spike is simply the derivative of the transmitted electron current which turns on abruptly at 0 eV. In our experience a resonant state near 0 eV or even slightly below causes the turn-on spike to be broadened. The sharpness of this feature in the present spectra supports our contention that the (π_4^*, π_5^*) splitting is very small in the chloro- and bromobenzenes. If the splitting between these two states were of the order of 0.5–1.0 eV, the lower energy state would give rise to attenuation of the electron current near 0 eV and a concomitant broadening of the turn-on feature in the derivative spectra. The dip which follows the spike at threshold is known as a "retarding cusp". It is a well-known instrumental artifact and has been investigated in detail by Johnston and Burrow.¹⁰ In the present case the retarding cusp introduces some uncertainty into our determination of the AE of the lowest energy

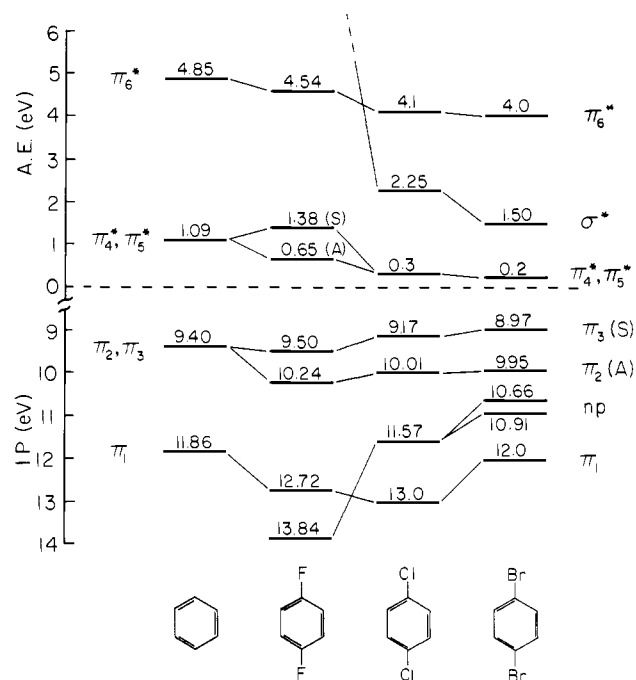


Figure 2. Correlation diagram giving the attachment energies (AE) and vertical ionization potentials (IP) of the para-dihalogen benzenes. The uncertainty in the AE's is ± 0.1 eV for measurements given to one decimal place and ± 0.05 eV for measurements given to two places. The IP's and their assignments are from ref 9.

resonance in 1,4-dichlorobenzene and 1,4-dibromobenzene.

To aid in the assignment of the resonant states observed in the dihalogen benzenes, SCF-MO calculations have been carried out. The results are presented in Table I. Since molecular orbital eigenvalues are not quantitatively equal to IP's or EA's even when large expansion basis sets are used, we employ minimal STO-3G bases¹¹ and expect only a qualitative reproduction of experimental trends. Standard carbon-halogen bond distances have been used and no alteration of the carbon-ring geometry has been considered. All calculations were done with use of the program GAMESS.¹² Our results for 1,4-difluorobenzene are identical with those of Millefiori,¹³ to within 0.1 eV.

Discussion

With respect to the electron-transmission spectra, two questions arise: What is the nature of the (π_4^*, π_5^*) splitting and what is the character of the intermediate resonance observed in the chloro- and bromobenzenes? Answers to both questions are suggested by theoretical calculations. Our SCF-MO calculations indicate that the splitting between the π_4^* and π_5^* virtual orbitals is somewhat larger in 1,4-difluorobenzene (0.4 eV) than in 1,4-dichlorobenzene (0.3 eV) and 1,4-dibromobenzene (0.1 eV). Our result for 1,4-difluorobenzene is consistent with the simple empirical model of Jordan and Burrow¹⁴ as well as the ab initio many-body calculation of Von Niessen et al.,¹⁵ which gives a splitting of 0.8 eV.

The splitting of the (π_4^*, π_5^*) pair in benzene which arises upon para substituted gives one orbital which is symmetric (S) and one which is antisymmetric (A) with respect to a plane perpendicular to the ring through carbons 1 and 4. For the antisymmetric orbital there can be no net resonance interaction between electron density

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in the π system of the ring and electron density at the substituent. There can be an inductive interaction which stabilizes both the antisymmetric and symmetric orbitals. Our calculations, as well as those of Von Niessen et al.¹⁵ and Jordan and Burrow,¹⁴ place the symmetric π^* orbital above the antisymmetric π^* orbital in 1,4-difluorobenzene as implied in Figure 2. This conclusion is at odds with an earlier assignment of similar data obtained by Frazier et al.¹⁶ Thus while both π_4^* and π_5^* are stabilized by an inductive interaction, the symmetric orbital is destabilized by a resonance interaction with occupied orbitals of substituent np character. This effect is most significant for a substituent from the first row of the periodic table. For the dichloro and dibromo compounds the average π_4^*, π_5^* energy is lowered compared to that of benzene in both calculation and experiment and the symmetric orbital is calculated to lie below the antisymmetric orbital. It is significant that the (π_4^*, π_5^*) splitting in 1,4-dibromobenzene is so small as to be unobservable while the (π_2, π_3) splitting is the largest in the series in both calculation and experiment. Splitting of π_2 and π_3 in the dibromo compound is expected to be large since the IP's of the π_2 and π_3 orbitals of benzene are only about 1.3 eV smaller than that for the predominantly Br 4p orbitals of 1,4-dibromobenzene (see Figure 2). However, the average $\pi_2, \pi_3 \rightarrow \pi_4^*, \pi_5^*$ singlet excitation in benzene is 6.3 eV¹⁷ so that the (π_4^*, π_5^*) - Br 4p energy difference is relatively large and the expected splitting is small.

An alternative assignment of the 0.65- and 1.38-eV resonance of 1,4-difluorobenzene based on continuum multiple scattering X α calculations has recently been given by Bloor and Sherrod.¹⁸ It was found that the π_4, π_5 orbitals are split by only 0.3 eV and that the S orbital gave very little electron-scattering intensity. These authors assigned the experimental resonance at 1.38 eV to diffuse d π orbitals which gave a surprisingly high scattering intensity. At present we cannot definitively choose between the two assignments. If the interpretation of Bloor and Sherrod is correct than the $\pi_4^* - \pi_5^*$ separation is not given by the peak separation in the electron-transmission spectrum. In any case, the single feature observed near the threshold for the dichloro and dibromo compounds must be assigned to π_4, π_5 . One useful step in settling this controversy will be a multiple scattering calculation on 1,4-dichlorobenzene to compare with the difluoro case. In any event, the interpretation of the ETS results may be less straightforward than commonly thought.

In our calculations on 1,4-dichlorobenzene and 1,4-dibromobenzene we identify one or more σ^* orbitals with eigenvalues intermediate between the π_4^*, π_5^* pair and π_6^* . We therefore assign the broad intermediate resonance in these two compounds to negative ion states arising from electron capture into σ^* orbitals. We have observed similar states in other 1,4-M(CH₃)_n-benzenes.^{2,3} In these compounds the σ^* orbitals apparently possess considerable M-CH₃ character and interact in a pseudo- π fashion with the benzene π system tending to stabilize the symmetric component of the (π_4^*, π_5^*) pair and destabilizing π_6^* . In the present case the π^* orbitals are localized at the carbon-halogen bond and by

symmetry cannot interact with the π system. C-Cl σ^* resonances have previously been identified in planar unsaturated hydrocarbons by Burrow et al.¹⁹

The electron-transmission spectra of the *p*-dihalobenzenes clearly imply that the inductive contribution of the halogen substituents has the dominant effect upon the π^* orbital energies. Interestingly the observed inductive effect of the halogens on the AE's associated with π_4^* and π_5^* increases on going down group 7 from F to Br in spite of the fact that the electronegativity increases on going up group 7. To understand the observed effect upon anion formation one must distinguish between the neutral atom electronegativity (that is, the tendency of a neutral atom to withdraw electrons) and the charge capacity. Since a negative ion is actually formed in these experiments, the important factor is the capacity to accommodate the extra electron. The results illustrate the well-known fact that the charge capacity of the halogens increases with atomic number.²⁰ Accordingly the EA of F is actually smaller than that of Cl. The inductive stabilization of π_4^* and π_5^* in going down the group is not observed for π_2 and π_3 . This is attributable to the inductive stabilization being offset by the destabilizing resonance interaction of the np lone pair with π_2 and π_3 .⁹

Comparison of our ETS results with other spectral quantities is not straightforward. It is well-known that the $\pi \rightarrow \pi^*$ (i.e., $\pi_2, \pi_3 \rightarrow \pi_4, \pi_5$) transitions in halobenzenes generally occur at lower energies than those in benzene itself and that the magnitude of the energy shift is F < Cl ~ Br.²¹ However, the expressions for $\pi \rightarrow \pi^*$ excitation energies within the MO framework involve significant electron repulsion integrals over MO's which may change appreciably from one halobenzene to the next so that a simple relationship of UV spectral energies and IP's and EA's is not found. A similar lack of correlation is found in comparing UV and electrochemical data for halobenzenes.²² Information on π^* orbitals is also available from electron energy loss spectra,²³ but correspondence with the ETS results is not straightforward. Even for benzene the electron energy loss spectrum²⁴ is interpreted as showing no feature corresponding to π_6^* which nevertheless appears clearly in the electron-transmission spectrum.²⁵

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Registry No. Benzene, 71-43-2; 1,4-difluorobenzene, 540-36-3; 1,4-dichlorobenzene, 106-46-7; 1,4-dibromobenzene, 106-37-6.

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