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**Author:** I. Novak, L. J. Harrison and W. Li  
**Author Address:** inovak@csu.edu.au  
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**Abstract:** The electronic structure of two isomeric dibromonaphthalenes (C10H6Br2) has been investigated by HeI/HeII photoelectron spectroscopy. The spectra were assigned by Green's functions calculations and comparison with the spectra of related dibromobenzenes (C6H4Br2). The analysis of π-orbital and halogen lone pair ionization energies, enabled us to determine the magnitude of bromine-bromine intramolecular interactions and distinguish between through-bond and through-space type interactions. We also discuss the halogen-halogen interactions in other polynuclear aromatics.  
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Keywords: photoelectron spectroscopy, substituent effects
Introduction

The substituent effects (SE) in naphthalene derivatives have not been studied by UV photoelectron spectroscopy (UPS) as extensively as those of their benzene analogues. UPS is an excellent experimental method for investigation of substituent effects. While monosubstituted naphthalenes have been studied by UPS [1,2], only a single study of disubstituted naphthalenes has been reported [3]. In some diiodonaphthalenes and diiodophenanthrenes distortions of the carbon skeleton were observed by X-ray diffraction [4]. The introduction of large halogens (bromine, iodine) into the aromatic skeleton at appropriate positions may induce molecular distortion. However, halogen substituents also serve as internal probes for the same distortion (in UPS), because halogen lone pair ionizations can be readily identified and measured accurately. In this work we shall discuss substituent effects in some dihalo aromatics (Scheme 1).

Experimental and Theoretical Methods

1,5-Dibromonaphthalene and 1,8-dibromonaphthalene were prepared according to the procedures reported previously [9,10]. Their identity and purity were checked by NMR and mass spectroscopy.

The sample inlet temperatures were in the range 90-100°C. These temperatures were necessary in order to obtain sufficient vapour pressure in the ionization region.
The HeI/HeII photoelectron spectra were recorded on a Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 meV and 70 meV, respectively when measured as FWHM of the 3p−1 2P3/2 Ar+ ← Ar (1S0) line. The resolution in the HeII spectra was always inferior to HeI, which implies that certain bands that are well resolved in HeI may become unresolved in the corresponding HeII spectrum.

The assignment of the spectra of large molecules can be facilitated by measuring relative band intensities at various photon energies. Band intensities of halogen lone pair ionizations depend strongly on photon energy. In particular, relative intensities of bromine lone pair bands decrease significantly (compared to carbon based orbitals) on going from HeI to HeII radiation. Such changes are caused by variations of Br4p and C2p atomic photoionization cross-sections with photon energy and are well substantiated by theoretical [5] and UPS [6] studies. These known intensity variations are an important assignment aid and they helped us to correlate bands with bromine lone pair ionizations.

The quantum chemical calculations were performed with the Gaussian 03 program [7a]. The full geometry optimization was performed using the Stuttgart effective core potential basis set for all atoms [7b]. The vibrational analysis performed on the optimized geometry revealed no imaginary frequencies thus confirming that the optimized geometry represents the true minimum on potential energy surface. Subsequently, a single point Green’s functions (OVGF) type calculation implemented in the Gaussian program was performed in order to obtain ionization energies. GF calculations were used previously to successfully assign the spectra of monohalobenzenes [8]. The optimized geometry for 1 was planar (C2v symmetry), unlike in the 1,8-diiodonaphthalene, because the bromine atoms are smaller than iodines and thus are not
subject to out-of-plane distortion. Some of the calculated and experimental geometry parameters are compared in Table 2.

**Results and Discussion**

The investigation of substituent effects requires reliable assignments of the spectra. Therefore we briefly describe the analysis of photoelectron spectra.

The HeI/HeII photoelectron spectra of 1 and 2 are shown in Figs. 1-2. In order to obtain reliable assignments, we combined the information on relative band intensities, band profiles, comparison with the spectra of bromonaphthalene [1] and dibromobenzenes [11], HeI/HeII variations of band intensities and theoretical methods (GF calculations). The comparison of ionization energies of 1 and 2 with reference molecules bromonaphthalene and dibromobenzenes (see Table 1 for ionization energies of reference molecules) suggests the energy ranges within which the $\pi$-ionizations and bromine lone pairs can be expected. The band profiles provide insight into the nature of the orbital from which ionization takes place; a sharp, narrow band often corresponds to the ionisation from strongly localized, nonbonding orbital as suggested by the Franck-Condon principle. Furthermore, bromine lone pair bands show a pronounced decrease in intensity on going from HeI to HeII photon energy. For example, the bands at 10.45 eV and 10.48 eV in the spectra of 1,5- and 1,8-dibromonaphthalene, respectively show this behaviour and thus can be readily assigned to bromine lone pair ionizations. Nevertheless, halogen lone pair bands sometimes overlap with other $\pi$ and $\sigma$ orbital ionizations which may mask the expected intensity changes. For example, the band at 9.75 eV in the spectrum of 1,8-dibromonaphthalene does not show such strong intensity decrease. This is due to the fact that the manifold is composed of two $\pi$-ionization and one bromine lone pair. The correlation with the reliably assigned spectra of bromonaphthalene and dibromobenzenes thus becomes necessary.
The assignments of the spectra of title molecules are given in Table 1 and were obtained by combining the arguments listed above.

The most important part of our analysis concerns the bromine-bromine interactions mediated via the aromatic π-system (through-bond; TB) or direct, through space interactions (TS). In 1 both TS and TB interactions are possible while in the 2 isomer only TB is applies. In order to deduce the magnitude of TS interactions we compare the molecular structures of 3 [4] and 1 [12]. Considerable distortion of iodines from the aromatic plane, due to halogen-halogen TS repulsion is evident in 3. However, 1 retains essentially planar geometry. Nonetheless, in 1 there is evidence of splaying i.e. Br-C1-C9 angles are increased to 127° which demonstrates that the halogens are pushed apart by TS interactions. It is interesting to note that the crystal structures of both compounds are complex: the crystal structure of 3 comprises six crystallographically independent molecules while the crystal structure of 1 shows disorder. This suggests that destabilizing, intramolecular halogen-halogen interactions may lead to disorder and complexity in their molecular and crystal structures. In support of this conjecture we recall that the crystal structure of 2 and 4 exhibit no disorder. In 4, the iodines are twisted strongly out of the plane of the aromatic system (by 63°) which is due to strong mutual repulsion (TS). However, this large strain also serves to “lock” the molecular geometry by making it more rigid. In 1 and 3 on the other hand, the destabilizing TS interactions are much weaker which enables molecules to relieve strain via different modes e.g. by splaying, changes in bond or torsion angles. We suggest that the existence of different modes of strain relief causes structural disorder and complexity.

What about the energy of destabilization in 1 which occurs as a result of TS halogen-halogen interactions? We shall estimate this energy from the halogen lone pair ionization energies. The energy ranges of bromine lone pair ionizations in 1 and 2 are 1.6 eV (11.35-9.75) and 0.6 eV
(11.05-10.45), respectively. The range comprises TS+TB interactions in 1 but only TB interaction in 2. We can thus estimate that Br-Br repulsive TS interaction has the magnitude of approximately 1 eV i.e. 96.5 kJ/mol. Surprisingly, in diiodonaphthalene analogues [3] similar method gave the estimate of iodine-iodine TS interaction as 0.6 eV i.e. 57.9 kJ/mol. This is contrary to the expectation that larger iodines will repel each other more strongly than the smaller bromines. The rationale for relative magnitudes of intramolecular interactions may be twofold. The distortion of iodines out of the aromatic plane in 3 leads to a reduction of TB $\pi$-interactions between iodine lone pairs (via aromatic $\pi$-system) as well to a reduction in the TS interaction. Splaying which takes place in 1 does not alter TB interactions significantly, but reduces the TS interaction only. Therefore, splaying appears to be less effective than the out-of-plane distortion for relieving spatial repulsions.

**Summary**

We have described the non-bonding, through-space interactions in dibromonaphthalenes. The UPS enabled us to estimate the energy of non-bonding interactions and compare it with the results for diiodonaphthalene analogues. The estimated intramolecular Br-Br TS interaction in 1 appears to be larger than the corresponding interaction in 3. It is normally expected that the smaller size of bromine atom compared to iodine leads to smaller intramolecular TS repulsion. This unexpected result was deduced from the UPS data and would be very difficult to obtain via other methods.

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References


Figure captions:
Fig. 1 Photoelectron spectra of 1
Fig. 2 Photoelectron spectra of 2
Fig. 2

HeII

HeI

Br

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