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Research paper

Substituent effects on cyclometalation: N-benzylideneanilines

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ABSTRACT

The electronic structures of several derivatives of N-benzylidenaniline ligands (NBA) studied previously by HeI UV photoelectron spectroscopy (UPS) have been re-analyzed with outer valence Green's function (OVGF) and ionization-potential equation of motion coupled cluster method (IP-EOMCC) quantum chemical calculations. The calculations allowed us to clearly identify molecular orbitals with predominantly nitrogen lone pair character and correlate their ionization energies with the experimental kinetic data on the cyclopalladation of imines. We have also rationalized the stability (or the lack of it) for NBA complexes with d-block transition metals.

1. Introduction

N-benzylideneanilines (NBA) studied in this work are examples of molecules with general formula R_3-N = CR_1R_2 belonging to the large family of compounds called Schiff bases [1,2]. They are in widespread use as antifungal, antibacterial, anti-inflammatory and antiviral agents. NBA are also of great importance as ligands in metal complexes which are used to activate C—H bonds in a variety of organic synthetic processes [3,4]. We shall focus in this work on the relationship between the electronic structure of NBA molecules and their chemical reactivity towards metals, especially as represented in cyclometalation reactions. The electronic structures of several NBA have been studied in the gas phase using HeI photoelectron spectroscopy [5,6]. However, in these studies low level semi-empirical quantum chemical methods like HMO or NDDO were used to analyse the spectra. The NBA compounds studied in this work are given in Fig. 1.

2. Experimental and computational methods

The details of the samples compounds 1–**12** studied and the conditions under which UPS measurements have been performed had been reported previously [5,6]. The experimental spectra are available in refs. 5 and 6 and have been reproduced in Supplementary Information. The quantum chemical calculations were performed with the Gaussian 09 program [7] and included full geometry optimization of neutral molecules at MP2/6-311G(d,p) level. This model chemistry was chosen because it reproduced well the molecular geometry and conformation of **1**, the only NBA molecule whose molecular structure has been studied experimentally. The structure of **1** was determined in the gas phase by electron diffraction [8]. The NBA molecules are non-planar with the ring A being twisted (by angle Θ_N) around C—N bond vs. the rest of the molecule which is planar. The vibrational analysis for each molecule confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized geometry was used as an input into the single point calculation using the outer-valence Green's function (OVGF) method and aug-cc-pVDZ basis set [9]. This method obviates the need for using Koopmans' approximation and provides vertical ionization energies with typical deviation of 0.3–0.5 eV (depending on the size of the basis set). We have used aug-cc-pVDZ basis set for all OVGF calculations. The increase in basis set size e.g. by going to aug-cc-pVTZ does not result in significantly improved ionization energies while it incurs steeply rising computational costs (Supplementary information). We have also tried to use higher-order correlated methods e.g. ionization-potential equation of motion coupled cluster method (IP-EOMCC) implemented in ORCA software [10] to calculate ionization energies, but no sufficient improvement in calculated values compared to OVGF was noted to justify increased computing resources required (Supplementary Information).

3. Results and discussion

3.1. Substituent effects on electronic structure

The HeI photoelectron spectra and their assignments are given in Supplementary Information. The most interesting information

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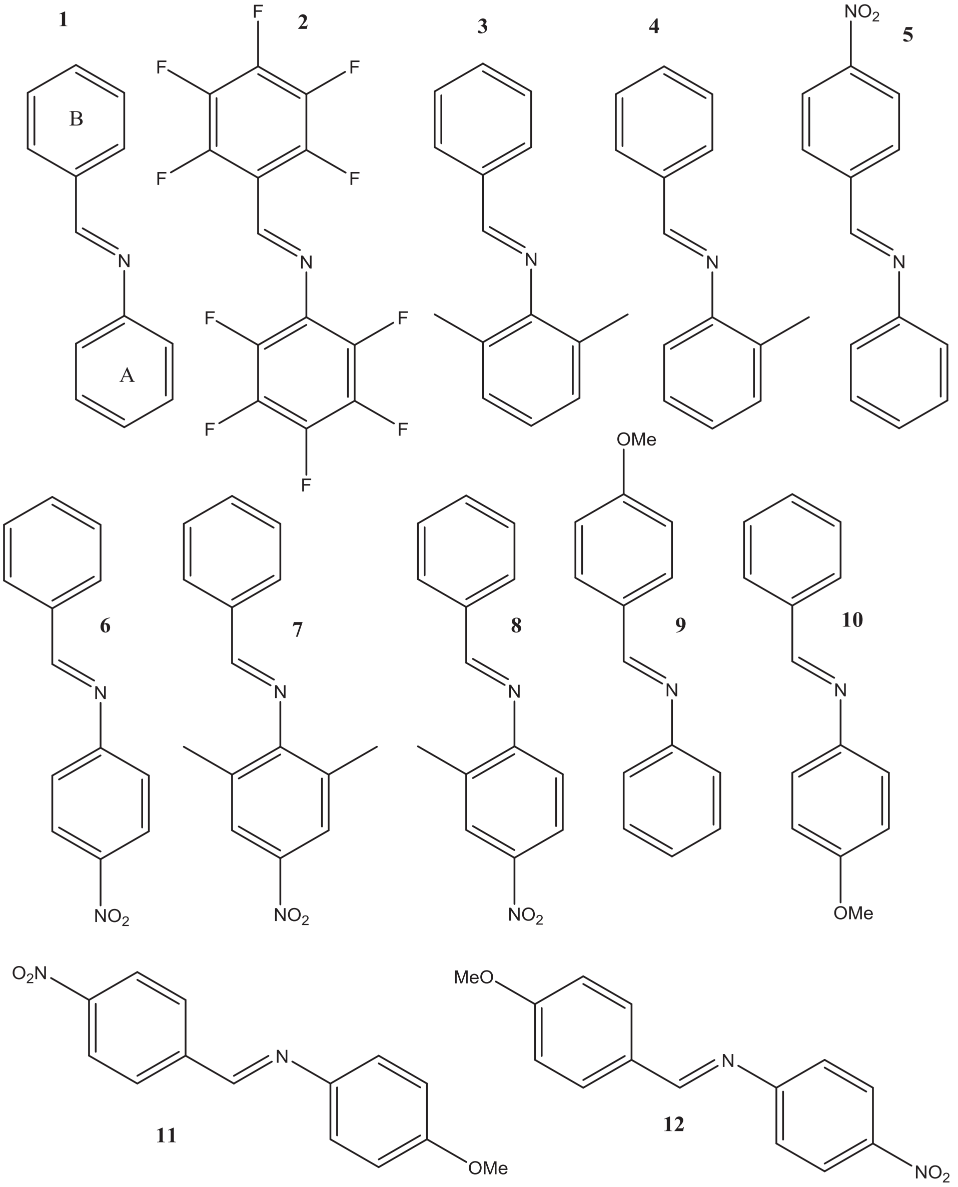

Fig. 1. Structures and N-benzylideneanilines studied and ring labeling convention.

concerning the spectra is the influence of substituents on the electronic structure of these aromatic molecules. We have selected two types of orbital ionizations to analyze substituent effects: HOMO and nitrogen lone pair (n_N) of the imine moiety. These two ionizations produce well resolved bands in the spectra whose ionization energies can be accurately measured in all cases. HOMO ionization comprises π-type orbital mostly delocalized over A ring with π_{CN} contribution from C=N (imine) moiety. The substituent effects are summarized in Table 1. The fluorine substituent is strongly inductively electron withdrawing (EW) and it stabilizes (increases orbital ionization energy) both HOMO and n_N to equal extent. Nitro substituent is also electron withdrawing (EW) by induction and by resonance mechanisms as can be gauged by comparing ionization energies of **1**, **5** and **6**. The EW effect is stronger on n_N than on HOMO (Table 1). The effect of OMe group is electron donating (ED) via both induction and resonance as can be seen from comparison of HOMO and n_N ionization energies in **1**, **9** and **10** (Table 1). The combined effect of OMe and nitro substituents (based on comparison of **1**, **11** and **12**) on orbital energies leads to very small changes in HOMO energy (EW and ED effects of the two groups approximately cancel out). However, we observe significant net EW stabilization of n_N as the result of presence of the two substituent groups. Why is there a different effect on π-type HOMO and σ-type n_N orbitals? OMe group is ED by resonance while nitro group is EW by resonance so that the electron density reduction at nitrogen atom by nitro substituent is approximately "compensated for" by ED of the methoxy group. This results in the small net effect. On the other hand, OMe and nitro substituents are both EW by induction so the n_N is stabilized by both substituents resulting in large EW effect (Table 1).

The effects of methyl substitution can be gauged by comparing HOMO and n_N ionization energies in two sets of molecules: **1, 3, 4** and **6, 7, 8**. As expected, the methyl groups exert weak, net inductive ED effect and destabilize HOMO and n_N orbitals; the destabilization is greater in dimethyl than in monomethyl derivatives (Table 1). Increased HOMO destabilization in **3** and **7** is due not only to the number of ED methyl groups present, but also to the larger Θ_N angle compared to **4** and **8**.