

Quantum-Chemical Study of the Structure of N-Substituted *p*-Quinonimines and Their Reactions with Hydrogen Halides

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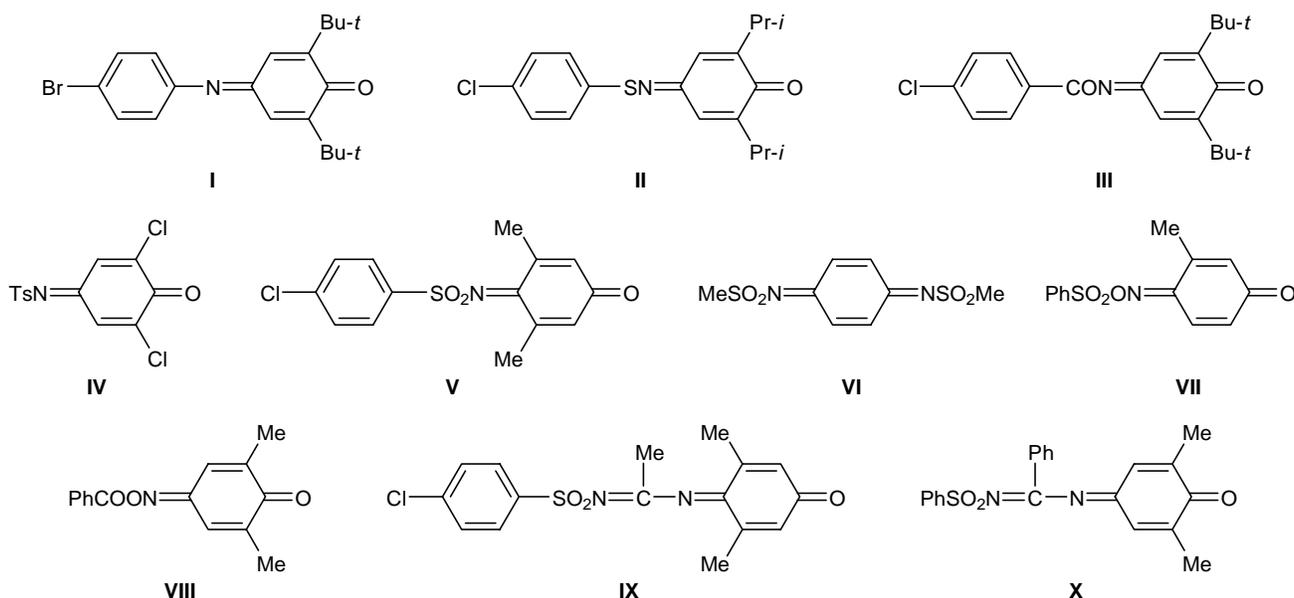
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Abstract—Quantum-chemical calculations and X-ray diffraction data for a series of N-substituted *p*-quinonimines showed that the PM3 method is the most suitable for determination of geometric parameters of these compounds. Moreover, it can be used to predict the site of addition of chlorine and bromine in the hydrohalogenation reaction.

Quantum-chemical methods are now widely used in studies on the reactivity of organic compounds. There are two main requirements to the level of approximation and choice of the calculation scheme. First, the results of calculations should be consistent with the corresponding experimental data, and second, the calculations should not be expensive from the viewpoint of computational time [1]. With the aid of MOPAC 6 software package which includes four semiempirical quantum-chemical methods (MINDO/3, MNDO,

AM1, and PM3) we made an attempt to find out which of the above procedures is most appropriate for N-substituted *p*-quinonimines, namely for determination of active centers in their molecules in nucleophilic addition reactions.

While analyzing the results obtained by any quantum-chemical method, the relative rather than absolute values are important. Therefore, the problem was to choose such a procedure which would ensure minimal deviations of the optimized geometric



parameters of various *N*-substituted *p*-quinonimines from the experimental data obtained by X-ray analysis. As a result, we could be able to compare the reactivity of these compounds and the position of reactive centers in their molecules.

Our previous studies have shown that the reactivity of quinonimines is strongly influenced by the bond angle at the imino nitrogen atom (C=N–X) [2]. We examined the dependence of the potential energy (*E*) of molecules **I–X** and their enthalpies of formation (ΔH_f) on the CNX angle. The X-ray diffraction data for compounds **I** [3], **II** [4], **III**, **X** [5], **IV** [6], **V** [2], **VI** [7], **VIII** [8], and **IX** [9] have already been reported. The calculations were performed by optimizing the other geometric parameters at a fixed CNX angle which was varied in the range from 100 to 180° through a step of 10°. Analysis of the results showed that the PM3 and MNDO methods give the most pronounced minima of *E* and ΔH_f at CNX angles similar to those found by X-ray analysis.

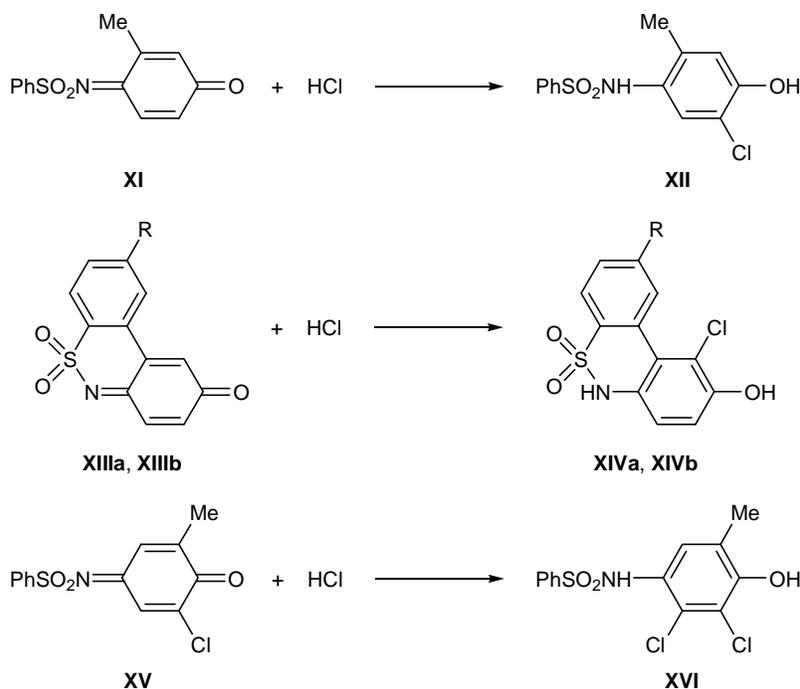
In order to elucidate in more detail the applicability of the above quantum-chemical methods for practical purposes we performed complete geometry optimization of molecules **I–X**. The least deviations of the calculated bond lengths and bond angles from the corresponding experimental parameters were obtained with the use of the PM3 procedure. The average deviations are as follows: bond lengths: 0.039 (MINDO/3),

0.032 (MNDO), 0.029 (AM1), 0.021 Å (PM3); bond angles: 6.365 (MINDO/3), 2.639 (MNDO), 4.755 (AM1), 2.608 deg (PM3).

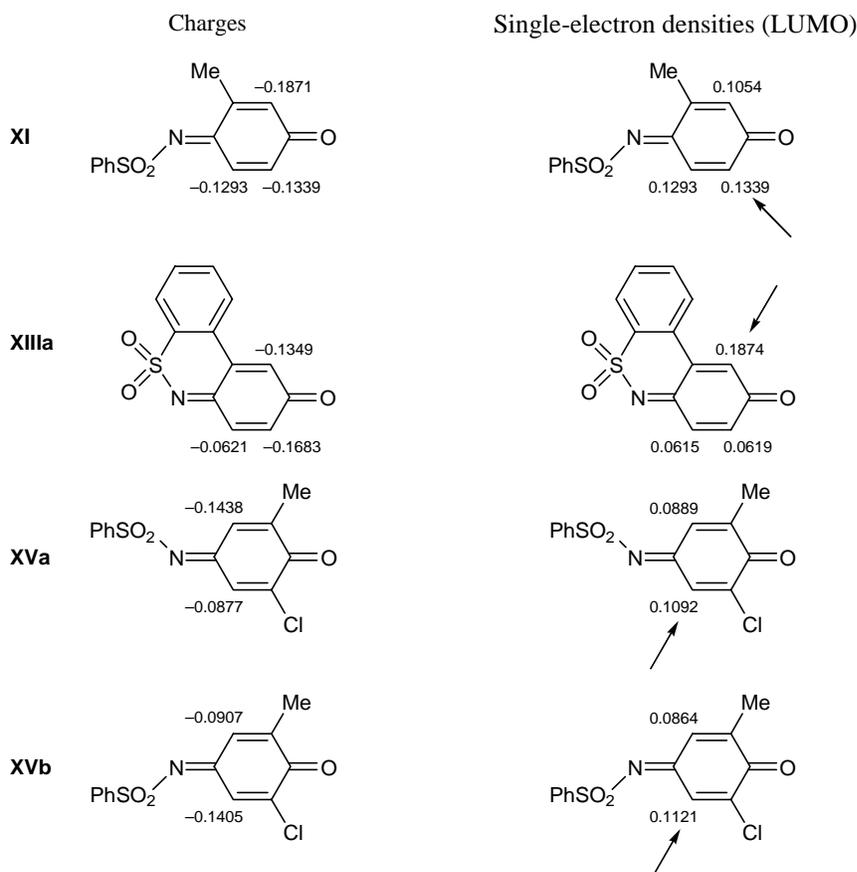
We previously showed that the site of addition of chlorine or bromine atom in reactions of quinonimines with hydrogen halides may be interpreted on the basis of PM3 calculations [10]. In the present work we continued studies in this line. Adams and Looker [12] were the first to report on the reaction of *N*-arylsulfonyl-1,4-benzoquinonimines with hydrogen chloride [11]; the authors formulated a rule which allowed prediction of the site of chlorine entry into the quinoid ring. According to this rule, protonation of the most basic center in the molecule occurs in the first step [12], and the subsequent attack by chloride ion on position 2 of the quinoid ring is followed by prototropic rearrangement. However, the rule does not work with *N,N'*-disubstituted 1,4-benzoquinonediimines in which different substituents have similar electron-acceptor or electron-donor properties.

Taking into account that hydrobromination and hydrochlorination of *N-p*-tolyl-1,4-benzoquinonimine results in chlorine addition at position 3, Burmistrov and co-workers [13–15] proposed a universal procedure for determination of the direction of hydrohalogenation on the basis of redox potentials. The procedure implied analysis of the thermodynamic stability of intermediate products having an *ortho*-quinoid

Scheme 1.



Scheme 2.



structure. However, experimental measurement of redox potentials of quinonimines is very difficult and laborious or even impossible. Furthermore, this redox procedure cannot be applied to some quinonimines because of specific structure of the quinoid ring.

We tried to solve the problem with the use of quantum-chemical calculations; in other words, we now propose an alternative procedure for prediction of the direction of hydrohalogenation of *p*-quinonimines. Our procedure properly describes the addition of HCl and HBr to various quinonimines having various substituents both at the nitrogen atom and in the quinoid ring. This method extends the potential of prediction of the site of halogen addition in hydrohalogenation and does not contradict the procedure based on redox potentials.

We were the first to effect hydrochlorination of compounds **XI**, **XIIIa**, **XIIIb**, and **XV**, which afforded addition products **XII**, **XIVa**, **XIVb**, and **XVI**, respectively (Scheme 1). The site of chlorine addition in these reactions cannot be predicted on the basis of redox potentials. Scheme 2 shows distribution of

charges and single-electron densities in molecules **XI**, **XIIIa**, **XV**, calculated by the PM3 method. The calculations were performed for both possible isomers of **XV**. It is seen that distribution of single-electron densities on carbon atoms in the quinoid ring is very consistent with the site of halogen addition observed experimentally (indicated by arrows). Chloride or bromide ion attacks that carbon atom of the quinoid ring, which possesses the highest single-electron density in the lowest unoccupied molecular orbital (LUMO). The LUMO energies of compounds **XI**, **XIIIa**, **XVa**, and **XVb**, calculated by the PM3 method, are -1.747 , -2.241 , -1.898 , and -1.886 , respectively; the HOMO energies of halide ions are -3.479 (Cl⁻) and -3.598 (Br⁻).

EXPERIMENTAL

Quantum-chemical calculations were performed on an AMD-K-6 PC using MOPAC 6 software package. The ¹H NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz) from solutions in CDCl₃; the chemical shifts were measured relative to TMS.

Hydrochlorination of 3-methyl-4-phenylsulfonylimino-2,5-cyclohexadienone (XI). Dry hydrogen chloride was passed through a solution of 7 mmol of compound **XI** in 10 ml of anhydrous chloroform until 2-chloro-5-methyl-4-phenylsulfonylamino-phenol (**XII**) separated as a colorless solid. Yield 93%, mp 136–137°C (from AcOH). Found, %: Cl 11.74, 11.86. $C_{13}H_{12}ClNO_3S$. Calculated, %: Cl 11.91. The structure of **XII** was proved by the 1H NMR spectrum of its oxidation product, 2-chloro-5-methyl-4-phenylsulfonylimino-2,5-cyclohexadienone, δ , ppm: 6.69 q (1H, 6-H), 8.40 s (1H, 3-H), 2.08 d (3H, CH_3).

Hydrochlorination of 2-R-9H-dibenzo[c,e][1,2]-thiazin-9-one 5,5-dioxides XIIIa and XIIIb. Dry hydrogen chloride was bubbled at 20–25°C through a solution of 4 mmol of quinonimine **XIIIa** or **XIIIb** in a mixture of 30 ml of benzene and 30 ml of acetone until the mixture turned colorless. The mixture was treated with charcoal and filtered, and the filtrate was evaporated under reduced pressure until a solid precipitated. The colorless precipitate was filtered off and recrystallized from benzene. Yield of **XIVa** 65%, mp 242–243°C. Found, %: N 4.73. $C_{12}H_8ClNO_3S$. Calculated, %: N 4.97. Yield of **XIVb** 73%, mp 238–240°C. Found, %: N 4.52. $C_{12}H_7Cl_2NO_3S$. Calculated, %: N 4.43. The 1H NMR spectra of **XIVa** and **XIVb** contained two doublets at δ 7.11–7.13 ppm (7-H) and 7.14–7.18 ppm (8-H), $J_{ortho} = 8.4$ – 8.7 Hz.

Hydrochlorination of 2-chloro-6-methyl-4-phenylsulfonylimino-2,5-cyclohexadienone (XV). Dry hydrogen chloride was passed through a solution of 2 mmol of compound **XV** in 5 ml of glacial acetic acid until the solution became colorless. The mixture was evaporated until colorless crystals precipitated. Yield of **XVI** 91%, mp 186–187°C [16].

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