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Semiempirical MO and voltammetric estimation of ionization potentials of organic pigments. Comparison to gas phase ultraviolet photoelectron spectroscopy

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Abstract

A number of organic pigments were identified by semiempirical molecular orbital calculations, using the PM3 method, as having ionization potential (IP) values of 7.0–9.5 eV. Based on photostability, solubility and commercial availability twelve (quinacridone, isoviolanthrone, indanthrone, indigo, 3,4,9,10 perylenetetracarboxylic dianhydride, bis(*p*-chlorophenyl)1,4-diketopyrrolo (3,4-C) pyrrole, pyranthrone, indanthrene yellow GCN, 16,17-dimethoxyviolanthrone, indanthrene gold orange, 4,4′-diamino-9,9′,10,10′-tetrone [1,1′ bianthracene], and *N,N*′ ditridecyl-3,4,9,10-perlenetetracarboxylic diimide) were chosen for further study. The accuracy of the MO calculations was confirmed by experimental measurement of the ionization potentials for eight of the pigments, using gas phase ultraviolet photoelectron spectroscopy. For compounds having at least three fused rings and containing oxygen, nitrogen, or both, the theoretical and experimental IPs have a linear relationship defined by the equation $\mathrm{IP}_{\mathrm{exp}} = 0.694\mathrm{IP}_{\mathrm{Calc}} + 1.9049$. Lewis acid pigment solubilization (LAPS) was shown to be a viable approach to preparing electrodes for cyclic voltammetry of pigment solid films. The results of the cyclic voltammetry experiments were utilized to formulate the equation E_{ox} (V vs. NHE) $= 0.5488\mathrm{IP}_{\mathrm{Calc}} - 3.042$, which relates the experimental oxidation potential to the theoretical IP.

Keywords: Pigments; Ionization potentials; Redox potentials; Molecular orbital calculations; Cyclic voltammetry; UPS

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1. Introduction

There are many reasons for the present interest in the ionization potentials (IPs) of organic compounds, including the use of such values to select appropriate materials for xerography, photography, or electroluminescence applications [1,2]. IP values are especially valuable when examining organic semiconductors for specific uses, since IP and electron affinity (EA) correspond to the valence and conduction band edges of the material, respectively. While the literature contains an abundance of IP data for organic compounds [3], little experimental data is available on the energy levels of large organic pigments.

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Pigments are primarily of interest in the coatings and plastics industries. For such applications, characteristics such as tinctorial strength, lightfastness and weatherability are more significant than IP or EA values. However, our interests involved making use of the insolubility and lightfastness of pigments for photoelectrochemical studies that also required a knowledge of the energy of the highest occupied molecular orbital (HOMO). IP and EA data can be used to develop an efficient, affordable, direct photoconversion scheme for generating H_2 and O_2 from H_2O using sunlight [4].

The preferred method for the direct measurement of gas phase IPs employs ultraviolet photoelectron spectroscopy. IPs are also related by Koopmans' theorem to the eigenvalues of the one-electron molecular orbitals obtained from theoretical calculations [5]. In addition, there are numerous commercial PC-based quantum chemistry software packages that employ semi-empirical MO methods to quickly and affordably calculate the energies of the HOMO and lowest unoccupied molecular orbital (LUMO) for molecules the size of a typical organic pigment.

With this is mind, our intent in the present work was to calculate HOMO energies for a series of related organic pigments and to assess the reliability of the calculated values by comparing them to experimental IPs and oxidation potentials determined via cyclic voltammetry. Calculations were performed using the widely available PM3 semi-empirical Hartree–Fock method as implemented in the CAChe desktop software package.

2. Experimental

2.1. MO calculations

Calculation of the HOMO and LUMO for each pigment was accomplished using CAChe® 3.0 software from Oxford Molecular Group, running on a 233 MHz Pentium II computer. The molecular structures were drawn within the input module of the program and the valence, hybridization, and initial geometry of each structure were corrected using the "beautify" option. After a preliminary geometry optimization by molecular mechanics (MM2) additional optimization was performed using PM3 parameters. The fully optimized structures were then submitted for PM3 calculation of the wavefunctions, including the HOMO and LUMO.

2.2. Ultraviolet photoelectron spectroscopy

The gas phase ultraviolet photoelectron spectra were recorded using previously described methods [6]. The argon $^2P_{3/2}$ ionization at 15.759 eV was used as an internal calibration lock of the absolute ionization energy, and the difference between the argon $^2P_{3/2}$ ionization and the methyl iodide $^2E_{1/2}$ ionization at 9.538 eV was used to calibrate the ionization energy scale. During data collection the instrument resolution (measured using FWHM of the argon $^2P_{3/2}$ peak) was 0.015–0.030 eV. Ionization peak positions were reproducible to ±0.02 eV.

2.3. Pigment solubilization

Solutions were prepared under an inert atmosphere in a glovebox. Using a process developed by Hsieh and Melnyk [7], 6 ml of nitromethane and 4 ml of methylene chloride were combined and 0.33 g of aluminum chloride was added. After stirring to dissolve the $AlCl_3$, 0.4 mmol of the pigment was added. The flasks were stoppered and the solutions were allowed to stir for 6–18 h.

2.4. Electrode preparation

The working electrode was a 1.0 cm^2 platinum foil. The electrode was passed through a hydrogen flame and then, under an inert atmosphere, was dipped in the pigment/nitromethane solution 1–7 times to form a visible coating, allowing time to dry between coats. After coating, the electrode was removed from the glove box and dipped in deionized water to remove any residual solvent mixture. It was then placed in a warm oven at approximately 110°C until dry.

2.5. Voltammetry

Voltammetric experiments were conducted using an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A, with data collected using a Hewlett Packard 7015B chart recorder. A three-electrode, single compartment configuration was used, with a platinum mesh counter electrode, and a Ag/AgClO$_4$ reference electrode. To convert the potentials to the more common normal hydrogen electrode (NHE) values, voltammograms were recorded for a ferrocene solution, first using a commercial saturated calomel electrode, SCE, and then the Ag/AgClO$_4$ electrode as the reference electrode. The Ag/AgClO$_4$ electrode was found to have a potential of $+0.043$ V when compared to the SCE. Therefore, 0.285 V was added to the potentials obtained using the Ag/AgClO$_4$, in order to reflect values obtained with an NHE.

Each scan was initiated at 0 V and the scan rate was 150 mV/s. Because the electrode coating eroded with prolonged cycling, the initial cycle was recorded rather than a steady-state cycle. If this initial scan showed irregularities, a new electrode was prepared and the experiment was repeated.

The voltammetry was performed in a mixture of 0.1 M tetraethylammonium perchlorate and DMSO when investigating reduction potentials, and 0.1 M LiClO$_4$ in acetonitrile was used as the medium for oxidation potential studies. The solvents (anhydrous) were obtained from Aldrich Chemicals and were used as received.

3. Results and discussion

The relationship between the oxidation–reduction, or redox, potentials and the ionization potentials–electron affinities (IP–EA) of molecules has long been recognized. Maccoll [8] first related redox potentials to the HOMO and LUMO energies of a molecule, and other researchers, including Dewar [9], have related redox potentials to IP–EA.

In order to select an initial group of pigments with which to conduct further studies, we performed MO calculations on a large number of pigments, looking for representatives having a calculated HOMO of 7.0–9.5 eV. The list of pigments was then narrowed to 12 candidates based on photostability, insolubility and commercial availability. Structures for the resultant pigments are shown in Table 1.

To confirm the accuracy of the MO calculations, eight of the pigments were analyzed by gas phase ultraviolet photoelectron spectroscopy. A comparison of calculated and experimental IP values is given in Table 2. Having previously conducted PM3 calculations on a number of compounds for which there were published IP values [10], it was anticipated that the experimental IP values would reflect higher HOMO energies than the calculated values. This hypothesis was confirmed, and similar results were obtained using the AM1 semi-empirical method. The AM1 method typically gave HOMO energies that were $\approx$1 eV lower than experimental values from gas phase IPs [11,12]. The experimental first ionization energies of the tested compounds varied from 6.78 eV for indanthrone to 8.22 eV for perylenetetracarboxylic dianhydride. The photoelectron spectrum of dimethoxyviolanthrone, rather than having well separated ionization bands, exhibited a continuum of ionizations of 7.6–11 eV, as shown in Fig. 1.

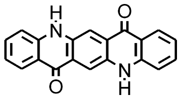
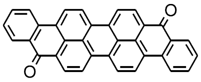
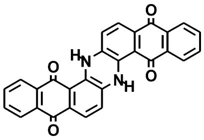
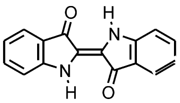
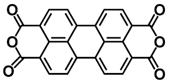
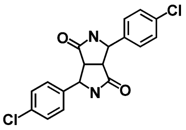
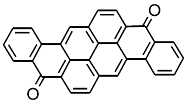
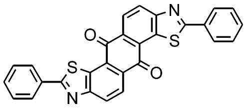
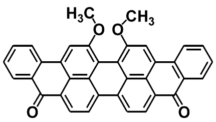
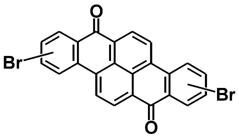
For a few of the pigments studied, the calculated HOMO energies were significantly lower than the experimental values. The differences between calculated and experimental ionization potentials were most pronounced for DPP and indigo. This may be due to their structural dissimilarity to the mostly fused ring structures comprising the other pigments. Indigo and DPP are the only compounds studied with five-membered rings, so that their parameter sets may not have adequately considered intermolecular π–π interactions. The presence of halogen atoms on DPP and indanthrene gold orange may also have caused greater than normal deviations.

To aid in the correlation of calculated and experimental IP values for future calculations involving similar compounds, a calibration curve for the theoretical versus experimental IPs was constructed. The resultant plot had a correlation coefficient of 0.8587. When the values for indigo and DPP were excluded from the calibration curve, Eq. (1) was derived, and the correlation coefficient improved to 0.9227.

$$\mathrm{IP}_{\mathrm{exp}} = 0.694\mathrm{IP}_{\mathrm{Calc}} + 1.9049 \tag{1}$$

As additional corroboration of the MO calculations and to define the relationships between the

Table 1
Pigments and structures

Pigment	Structure
Quinacridone	
Isoviolanthrone	
Indanthrone	
Indigo	
3,4,9,10-Perylenetetracarboxylic dianhydride	
Bis(*p*-chlorophenyl)1,4-diketopyrrolo (3,4-C) pyrrole (DPP)	
Pyranthrone	
Indanthrene Yellow GCN	
16,17-Dimethoxyviolanthrone	
Indanthrene Gold Orange	

(*continued on next page*)

Table 1 (*continued*)

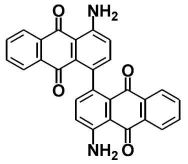
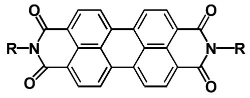
Pigment	Structure
4,4′-Diamino-9,9′,10,10′-tetrone [1,1′ bianthracene] (Pigment Red 177)	
N,N′ ditridecyl-3,4,9,10-perylenetetracarboxylic diimide (perylene diimide)	

Table 2
Ionization and redox potentials

Pigment	IP_{calc}	IP_{exp}	E_{red} (vs NHE)	E_{ox} (vs NHE)
Quinacridone	7.65	7.23	−1.11	1.39
Isoviolanthrone	8.22	7.87	−0.34	1.54
Indanthrone	7.25	6.78	−0.29	0.99
Indigo	8.34	7.23	−0.37	1.19
Perylenetetracarboxylic dianhydride	9.31	8.22	−0.05	2.29
DPP	8.50	7.47	−0.70	1.49
Pyranthrone	8.54	NA	−0.30	1.39
Indanthrene Yellow	9.41	NA	NA	1.09
Dimethoxyviolanthrone	7.90	> 7.60	−0.34	1.16
Indanthrene Gold Orange	8.84	8.07	−0.03	1.50
Pigment Red 177	8.21	NA	−0.56	1.32
Perylene diimide	8.87	NA	−0.14	2.09

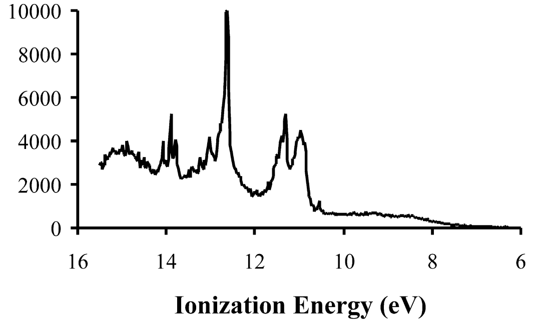


Fig. 1. Ultraviolet photoelectron spectrum of dimethoxyviolanthrone.

gas phase and solid phase energy levels, experimental redox potentials were determined and are also listed in Table 2. While voltammetry is more frequently conducted with the electroactive species dissolved in water or an organic solvent, solid state or thin film voltammetry is becoming more widely used [13–16]. In the present research, redox potentials were determined in the solid state because of low pigment solubility and because the intended end use of these pigments involved the solid state.

Hsieh and Melnyk developed Lewis acid pigment solubilization, LAPS [7] for the fabrication of multilayered organic photoconductors. Initially, we had planned to use pigment solutions to conduct solution voltammetry; however, the nitromethane used in the solubilization technique reacted with $AlCl_3$ to form the electroactive nitrosyl cation, complicating the electrochemistry [17,18]. Although it was not possible to use the pigment/nitromethane solutions to do electrochemistry, these solutions were useful for coating electrodes for thin film voltammetry.

The reductions were easily obtained although, in many cases, the wave exhibited a shoulder that was due to the adsorbed and solution phases of the pigments [19]. It was especially interesting to note that while the parent pigments were virtually insoluble in DMSO, the reduced forms were more soluble in this solvent. During the potential sweep, the pigments slowly dissolved from the electrode. Frequently, the solvent surrounding the electrode (and sometimes the electrode coating) developed a different color from the original pigment, as observed with the reduction of vat dyes. For instance, during the voltammetry with the dark blue pigment isoviolanthrone, the solution surrounding the electrode became rose-colored. A sample of isoviolanthrone added to fresh DMSO was not soluble and no color appeared in solution, providing evidence that only the reduced form was soluble.

The voltammetry experiments that were conducted to determine the oxidation potentials were more difficult than the reductions. Several compounds gave quasi-reversible voltammograms in which the peaks were of equal size but whose separation was far greater than the 59 mV expected for a reversible oxidation. A representative voltammogram can be seen in Fig. 2 for dimethoxyviolanthrone. Others, on reversal, had cathodic waves that were either absent or very small (see Fig. 3), an indication that the cation radical undergoes a rapid chemical reaction after electron transfer [20] or that the charge transfer rate is slow. Unlike the solubility behavior observed following reductions, the oxidized species were insoluble. The peak potentials for the irreversible oxidations were corrected by subtracting 0.15 V, to give an approximation of the oxidation potential [21].

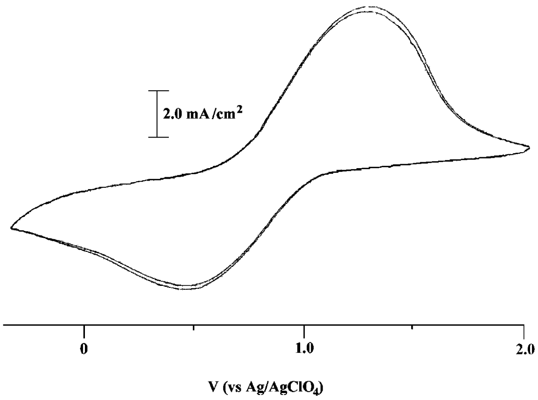


Fig. 2. Cyclic voltammogram for the oxidation of dimethoxyviolanthrone.

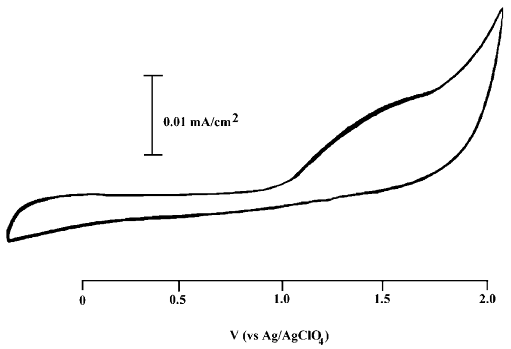


Fig. 3. Cyclic voltammogram for the oxidation of bis (*p*-chlorophenyl) DPP.

The difficulties encountered in obtaining oxidation potentials emphasized the advantages of having a method for obtaining the desired data, even when the resultant cation is unstable. It is reasonable, therefore, to investigate the relationship between calculated IPs and experimental oxidation potentials, as a way to approximate the oxidation potential. A number of researchers [21–23] have discussed the rationale for equating the two values and have shown that a useful relationship exists. The equations developed, however, are valid only for structurally similar compounds, because the constants in the equations take into account differences in the solvation energies of the oxidized species and the parent molecule, as well as the potential of the reference electrode. Changes in geometry that could occur when an electron is removed during the slow time scale of a voltammetry experiment can also cause experimental oxidation potentials to differ from the calculated, frozen geometry HOMO energies. An analysis of the calculated IP and experimental E_{ox} data obtained in our study gave Eq. (2), which can only be used for determining oxidation potentials for closely related compounds in the solid state.

$$E_{ox}\ (V\ vs.\ NHE) = 0.5488IP - 3.042 \quad R^2 = 0.7285 \tag{2}$$

The dissimilar compounds, indigo and DPP, again were excluded from the calibration curve, as was indanthrene yellow, the only sulfur containing compound. Including these compounds dramatically decreased the correlation coefficient to 0.2890. The complete listing of redox potentials, theoretical ionization potentials and experimental ionization potentials are shown in Table 2.

4. Conclusion

In this work, we have developed equations that correlate the results of MO calculations to the experimentally determined ionization and oxidation potentials of organic pigments that have at least three fused rings and contain oxygen, nitrogen, or both. These equations may be used to estimate the IP or oxidation potential of additional pigments having similar molecular structures. Furthermore, we have demonstrated that LAPS can be used as a technique to prepare thin film electrodes for cyclic voltammetry.

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