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The Relationship between Redox Potentials and Torsional Angles in 4,4'-Dimethyl N, N'-Alkylidene 2,2'-Bipyridinium Salts

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Abstract: The redox potentials of 4,4'-dimethyl-N'N'-alkylidene bridged 2,2'-bipyridinium salts derivatives (DBPAs) can be controlled by changing the N, N'-alkylidene bridge length which changes the conformation of the DBPAs.. In this paper, the torsional angles between the two pyridine rings and the molecular energy of DBPAs are calculated using a PC based software package (AccuModel 1.2). The relationship between torsional angle and N, N'-alkylidene bridge length is discussed. The molecular energy of DBPAs can also be related to the torsional angles (or N, N'-alkylidene bridge size). Some DBPAs had been synthesized and their redox potentials measured. The difference in potential between ethylene and propylene bridged DBPAs is large enough to make a organic diode through bilayer modified electrode.

Keywords: 4,4'-dimethyl-2,2'-bipyridine N,N'-alkylene derivatives, energy minimization, calculation of geometry parameters.

Introduction

Bilayer modified electrodes with an unidirectional electron flow property are of interest for their potential use in understanding energy transfer in plants or animals and their applications for the preparation of organic solar cells. Some chemical sensors, molecular electron devices and organic

photocells based on this kind of structure had been built and used in various applications [1]. This kind of diode-like device can be prepared using two electroactive polymers with different redox potentials through a sequential modification of the electrode surface. The unidirectional electron flow property can be built in this structure because the electron can only move from the polymer with the higher redox potential to the polymer with the lower one during the redox reaction (within some potential range). The reverse route is forbidden. It is clear then that the most important factor for making such a structure is to find or synthesize the two required polymeric modifers with a suitable redox potential difference and good reversibility during the redox reaction. In our previous work, a redox potential difference on the same redox center was obtained by three methods [2-4]:

1). The redox center is substituted with substituents of different electronegativity;

2). The conjugated system in the redox center is extended by substitution or another method, and

3). By changing the conformation of the redox molecule.

In first case, the electron density on the redox center is affected by the substituents present, as the redox potentials of the resultant chemicals depend on the electron density. In this case, the negativity difference between two substituents is important. In second case, the larger conjugated system usually is easier to reduce than smaller one, so a redox potential difference can be created. In this paper, we wish to discuss the third case, to probe the effects of conformation changes of the redox system and see it how they influence the redox potential.

The bipyridine derivatives salts (4, 4- or 2, 2'-bipyridinium salts) are considered to be good redox centers because of the nearly complete reversibility of their redox reactions. We found that 2, 2'-bipyridine derivatives could react with alkyl dibromides to form N, N'-alkylidene bridged bis-salt derivatives and that these also display good reversibility. It is very interesting to note that their redox potentials depend on the length of alkylidene chain [5]. When we used 1, 2-dibromoethane and 1, 3-dibromopropane reacted with 4, 4'-dimethyl-2, 2'-bipyridine respectively, the resulting DBPA compounds (Figure 1) show redox potentials of 0.44 V and 0.66 V vs SCE respectively. The redox potential difference is 0.22 volt and this is big enough to form an organic diode [6].
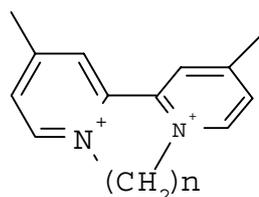
Figure 1. DBPA structures (the torsional angle formed by the N,N'-alkylidene bridge).

We studied these phenomena using molecular models and computation of the molecular structure, finding that their dipole moments and electron densities are nearly same, and the conjugated systems of the molecular structures are also not extended. The only distinct difference is their conformation that have different torsional angles between two pyridine rings. It is clear then, that the torsional angle is formed and controlled by the N, N'-alkylidene bridge between two nitrogen atoms. However, this

torsional angle could destroy the conjugation between the two pyridine rings and reduce their stability to some extent, so the electric charge cannot be shared properly throughout the whole molecule during the reduction reaction. In any case, the conclusion that the redox potential is dependent on the torsional angle can be made from the analysis. This qualitative conclusion was received widely and is confirmed by many experiments [5, 6, 7]. In this paper a computational method quantitative analysis of the relationship between the redox potentials and the torsional angles in this kind of system will be carried out by the energy minimization and measurement of torsional angles.

Results and Discussion

The geometric and energy parameters (structure, torsional angle, dipole moment and total energy) of five 4, 4' –dimethyl-2, 2'-bipyridine N, N'-alkylidene bridged derivatives molecules are listed in the Table 1. The molecules **1** and **2** have been synthesized and their redox potentials have been measured; those of the other molecules have not been determined yet. The torsional angles were measured by choosing four atoms in sequence on two pyridine rings and assuming all six atoms of pyridine are in one plane. The redox potentials were measured by cyclic voltammetry (at υ= 0.1 V/s, in 0.1 m $Bu_4N(ClO_4)$/MeCN, SCE as reference).

Table 1. Molecular structures and torsional angles.

No	Molecule Structure	Torsional angle (degrees)	Redox potential (measured) (volts vs. SCE)	Dipole moment	Total energy (kcal/mol)
1		0.02		0.0797	36
2		14.07	0.44	0.0219	37.8
3		27.30	0.66	0.0435	58.6
4		49.27		0.0677	68.1
5		49.60		0.0208	78.5
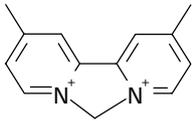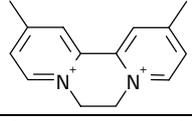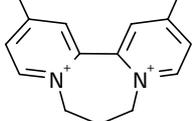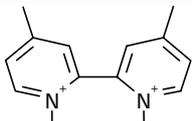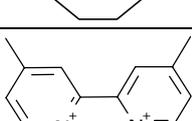
It can be seen from Table 1, the dipole moments for all molecules vary in the range 0.0208 to 0.0797. The measured torsional angles of DBPAs are 0.02, 14.07, 27.30, 49.27 and 49.60 degree respectively, corresponding to N, N'-alkylidene bridge C-atom numbers of 1, 2, 3, 4, and 5. These differences are quite distinctive. The longer the bridge is, the larger the torsional angle becomes when N, N'-bridges are 1 to 4 carbons in length. When the bridge length increases to 5 carbon (pentylene), the torsional angle does not increase further. The plot of torsional angles vs N, N'-alkylene bridge size was shown in Figure 2. The relationship between torsional angle and N, N'-alkylidene bridge is nearly linear for the first four molecules.
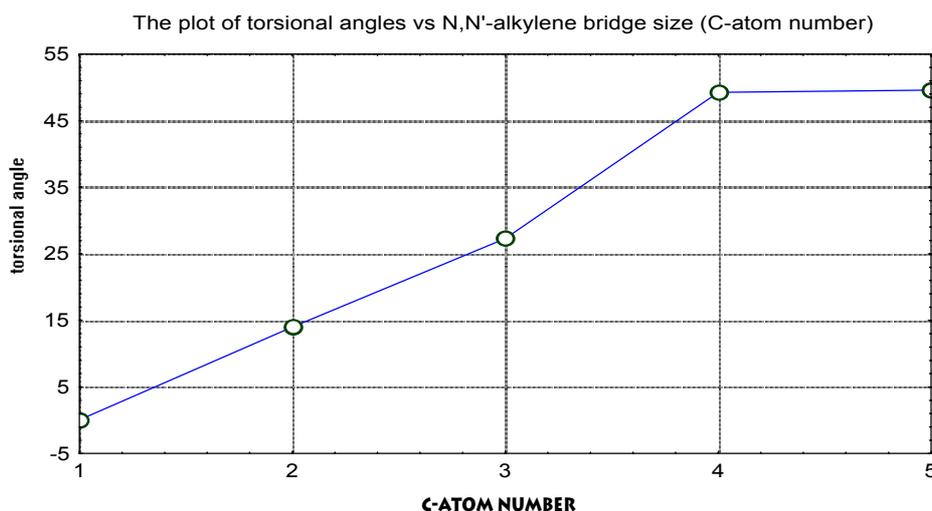
Figure 2. The relationship of torsional angle and N, N'-alkylidene bridge in DBPAs.

The total energy of the DBPA molecules also varies with the N, N'-alkylidene bridge length. The total energies measured are 36.0, 37.8, 58.6, 68.1 and 78.5 kcal/mol, respectively, corresponding to N, N'-alkylidene bridge C-atom numbers of 1, 2, 3, 4, and 5. The plot of these parameters vs C-atom number is shown in Figure 3.
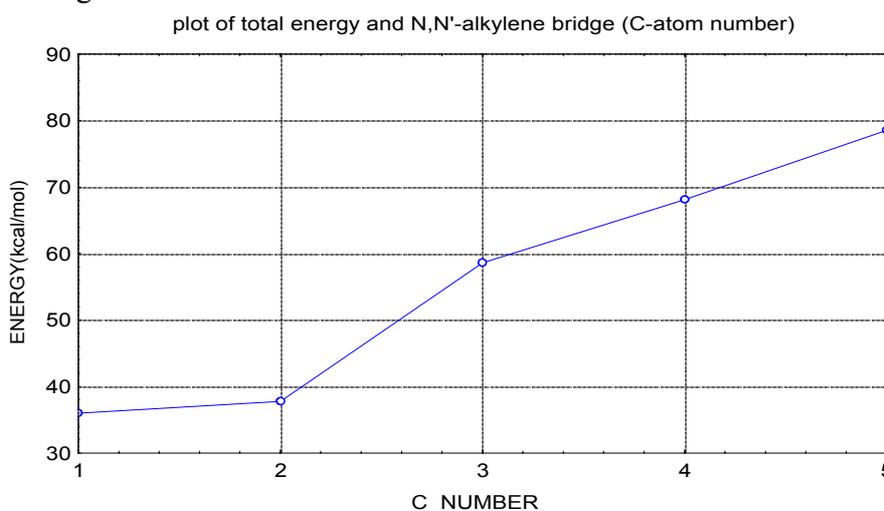
Figure 3. The relationship between molecular energy and N, N'-alkylidene bridge size.

The molecular energy in the DBPAs increases with C-atom number for all five molecules studied in this case. The higher molecular energy may mean that they are more difficult to reduce according to the experiment results. If the molecular energy of DBPAs in the first reduced state could be obtained by some means, we should have a way to calculate the redox potentials directly. Unfortunately, we cannot calculate the molecular energies of DBPAs in the reduced state using *AccuModel 1.2* because we do not know the exact molecular structure in this state. We assume that the two pyridine rings should be coplanar to share the unpaired electron in the reduced state efficiently. Thus we can say that N, N'-butylene or pentylene bridge DBPAs derivatives should have a more negative reduction potential. They may be used together with the N, N'-ethylene bridged DBPA to form a redox pair to make an organic diode with a larger electric gap.

Experimental

Molecular structure building, energy minimization and geometry parameters measurement with AccuModel 1.2

The *Accumodel 1.2* (MicroSimulation Inc.) software package was used to build the molecular structure models on a PC. The conformations of molecular structures were determined through an energy minimization method (structure optimization). In this case, the molecule should have a lowest energy and stay in a stable state. The conditions of energy minimization are shown in Table 2.

Table 2. The conditions of energy minimization.

Minimization method	Steepest Descent method
Maximum number of calculation	1000
Number of Steps Between Screen Change	5
Convergency criterion (RMS force)	0.05
Initial Step	0.0005
Applied force field	MM3 + UFF(Universal force field)

The geometry parameters and total energies of these molecules were measured and the operation included four steps:

1). Building of a molecular model using *Accumodel 1.2* .

2). An energy minimization operation to obtain a molecular structure in the lowest energy level was performed.

3). Torsional angles between two pyridine rings and the total energy was calculated.

4). Other geometry and electronic parameters of the molecular models was calculated.

Synthesis of 4, 4' –dimethyl, N, N'-ethylene-2, 2'-bipyridine (1) and 4, 4' –dimethyl, N, N'-propylene 2, 2'-bipyridine(2)

4, 4' –dimethyl, N, N'-ethylene-2, 2'-bipyridine(1): 368mg of 4,4'-dimethyl-2,2-bipyridine (Fluka, Puriss) was dissolved in 5 ml 1,2-dibromoethane (fluka, p.a) and stirred under N_2 at 100 ^OC for 20 hours. The resulting precipitate was filtered and successively washed with Et_2O and hexane, respectively. After drying overnight under vacuum at room temperature, 740 mg of 4, 4' –dimethyl, N, N'-ethylene-2, 2'-bipyridine(**1**) was obtained at a light yellow powder. ^{1}H-NMR (90MHz, D_2O): 2.90 (s, 3H), 5.20(s, 4H), 6.20(t, 2H), 6.9(t, 2H), 8.3(t, 2H).

4, 4' –dimethyl, N, N'-propylene-2, 2'-bipyridine(2): 368mg 4,4'-dimethyl-2,2-bipyridine (Fluka, Puriss) was dissolved in 5 ml 1,3-dibromoethane (fluka, 98%) and stirred under N_2 at 100 ^OC for 20 hours. The resulting precipitate was filtered and washed successively with Et_2O and hexane, respectively. After drying overnight under vacuum at room temprature, 780 mg of 4, 4' –dimethyl, N, N'-propylene-2, 2'-bipyridine(**2**) were obtained at a light yellow powder. ^{1}H-NMR (90MHz, D_2O): 2.90 (s, 3H), 4.20-5.20(m, 6H), 6.20(t, 2H), 6.9(t, 2H), 8.3(t, 2H).

Cyclic Voltammograms:

A XJP-821(B) Polargraph was used as potentiostat/function Generator and a Dahua-LZ3-100 XY-recorder was used to record the voltammograms. Working electrode: Glassy carbon electrode, Reference electrode: SCE, Counter electrode: Pt-wire. Scan rate: 100 mV/S, between 0 V and −1.0V.

Acknowledgements

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Sample Availability: Samples are available from the authors.