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OXIDATION POTENTIALS OF 1,2,3,4-DIBENZO[2.2.3]CYCLAZINES, PERIPHERAL 18π ELECTRON SYSTEMS[§]

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Abstract-Cyclic voltammetry of 1,2,3,4-dibenzo[2.2.3]cyclazine and its derivatives was carried out to support the previous observation of the cation radicals in these compounds. The observed oxidation potentials are compatible with the HOMO level instability arising from the introduction of the dibenzo-group in [2.2.3]cyclazine, as was presumed by the ESR observation.

Peripheral conjugate heterocyclic systems such as bridged heteroannulenes and cyclazines have attracted considerable attention regarding their stability and π-electron delocalizations.[1] [2.2.3]Cyclazine(**1**)[2] is a typical example, giving peripheral 10π electron conjugate. Previously we have reported the first observation of the cation radicals from the [2.2.3]cyclazine system in which two benzene rings are annulated at 1,2,3,4 positions, e.g. 1,2,3,4-dibenzo[2.2.3]cyclazine (**2a**).[3] In contrast to **1**,[4] cation radical species can be readily generated from **2a** upon oxidation with $AgClO_4$, whereas attempts to form stable anion radicals as in **1** were unsuccessful. These facts were explained, based on the HOMO and LUMO energy-level shifts influenced by extending the conjugate system. It was pointed out that, according to the MO calculations, both HOMO and LUMO energy levels of **2a** shift upward as compared to those of **1**, in qualitative agreement with easier oxidation and harder reduction of **2a** than **1**.

This communication reports the oxidation-reduction potentials of **2a** and its derivatives as studied by cyclic voltammetry (CV) in order to ascertain the abovementioned qualitative discussions. As the derivatives of **2a**, several electron-

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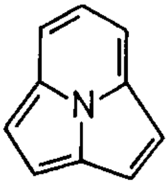
[§] Dedicated to Professor Rolf Huisgen on the occasion of his 70th birthday.



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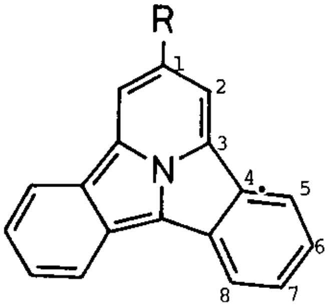

2a, R=H

2b, R=D

2c, $R=CH_3$

2d, $R=C_6H_5CO$

2e, $R=C_6H_5$

Table 1. Oxidation Potentials

2a	+0.70 V
2b	+0.69 V
2c	+0.59 V
2d	+0.85 V
2e	+0.64 V

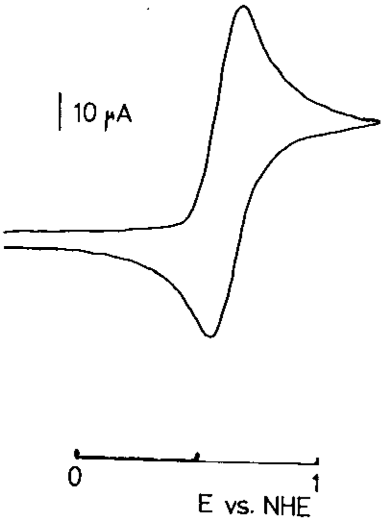

Figure 1. Cyclic voltammogram of **2a** in acetonitrile.

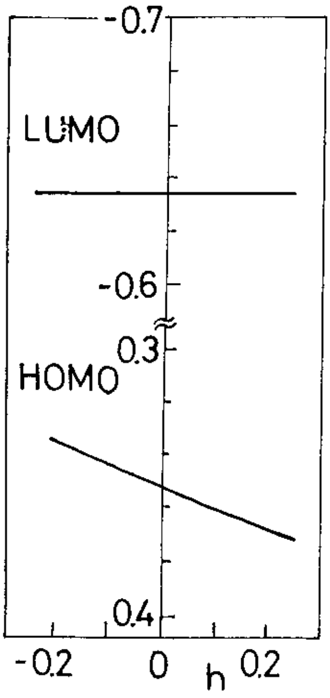

Figure 2. Energy variations of HOMO and LUMO levels in the units of β.

donating or -withdrawing groups were introduced at the position 1[5] (R=D, **2b**, R=CH_3, **2c**, R=C_6H_5CO, **2d**, R=C_6H_5, **2e**)[6] and their CV measurements were carried out.[7] Purified and dried acetonitrile and tetra-n-propylammonium perchlorate of special grade for polarography were used as a solvent and a supporting electrolyte, respectively. In order to avoid the ambiguity of the potential of the reference electrode in the CV measurements, a small amount of ferrocene was added and the position of the waves of the compounds under consideration was directly compared to that of ferrocenium/ferrocene peak (0.400 V vs. NHE) as an internal standard.[8] Figure 1 is a voltammogram of **2a**, showing a very low oxidation peak, +0.70 V vs. NHE. Sweeping towards a reductive area up to -1.2 V exhibited no appreciable wave. These facts indicate that **2a** is easily oxidized and is rather hard to reduce, supporting the observation of the cation radical species in **2a** and **2c** reported in the previous communication.[3]

HMO calculations disclosed the HOMO and LUMO energy to be 0.352 and -0.635, respectively, in the units of the carbon resonance integral β.[3] These are the considerable increases from the HOMO (0.580β) and LUMO (-0.594β) levels of **1**. Especially the instability of the HOMO level is appreciable. The unpaired electron distribution determined from the previous ESR measurements shows a fair amount of delocalization to the peripheral conjugate system, particularly on the dibenzo-group.[3] The CV and ESR results imply the characteristic behaviors of **2a** due to the large (18π) peripheral conjugate system, e.g. due to the significant perturbation by the dibenzo-group.

Each oxidation potential for the compounds(**2a-e**) is summarized in Table 1, which shows remarkably large effect of the substituents, ranging from +0.59 to +0.85 V vs. NHE. This substituent effect may be related to the fact that the proton hyperfine coupling constant at the substituted position, that is, the position 1 is the largest.[3] The electron-donating or electron-withdrawing quality of the substituent at the position 1 seems to influence essentially on the HOMO energy levels of **2a-e**. Actually this is evidenced by the MO calculations, taking into consideration the change of the Coulomb integral α of the carbon atom attached to the substituent, that is,

$$\alpha = \alpha_0 + h\beta$$

Here α_0 and β are the usual Coulomb- and resonance-integral parameters in the MO calculations, respectively. The parameter h was changed between -0.2 to +0.2, depending on the electron-donating or electron-withdrawing substituents. The HOMO and LUMO energy variations based on the HMO calculations are shown in Figure 2, which indicates the higher instability of the HOMO energy level, that is, the easier oxidation for the electron-donating substituents ($h < 0$). On the other hand, the HOMO energy level is greatly stabilized for the electron-withdrawing substituents ($h > 0$), resulting in the large oxidation potentials.

In the previous work,[3] it was concluded that the characteristic behavior of **2a** is apparently due to the large (18π) peripheral conjugate systems, e.g. due to the significant perturbation of the dibenzo-group. The present CV work not only supports the characteristic behavior of **2a** but also discloses the low oxidation potentials and the great substituent effect of the position 1. These results, together with the unpaired electron distribution in the cation radicals of **2a-e**, belong to the characteristic physical-organic properties of the 1,2,3,4-dibenzo-[2.2.3]cyclazine and would shed light on the peripheral 18π electron structure, which will be discussed elsewhere.[9]

REFERENCES AND NOTES

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