硝基芳烃对斜生栅列藻的毒性与结构相关性研究*

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摘要　采用量子化学 MNDO 法计算了 18 种硝基芳烃化合物的分子量低空轨道能（E_{LUMO}），分子最高占有轨道能（E_{HOMO}），生成热之差 $\Delta(\Delta H_f)$，偶极矩 μ 及净电荷 Q_{-NO_2}。用这 5 种量化参数对斜生栅列藻的急性毒性值进行定量构效关系（QSAR）研究，得到如下 3 参数方程：$-\log EC_{50}=2.92-0.077\Delta(\Delta H_f)+0.08\mu+0.28\ E_{HOMO}$，$n=18$，$r=0.961$，$S=0.173$。应用所得方程计算了所研究系列化合物的毒性，讨论了各类化合物的毒性作用。

关键词　硝基芳烃，量化参数，毒性，QSAR 方程。

硝基芳烃化合物是一类重要的环境污染物，在江水中检出率很高，其中的硝基苯，2，4-二硝基甲苯及 2，6-二硝基甲苯是美国 EPA 的优先监测物。因此，研究这类化合物的结构与毒性的关系，以推测其环境行为是非常重要的。近年来，随着电子计算机的发展，各种量化方法在构效关系中已得到越来越广泛的使用。本文在前人工作的基础上，使用量子化学 MNDO 法计算了系列硝基芳烃的 5 种量化参数，并用统计分析方法对斜生栅列藻的急性毒性值进行 QSAR 研究，得到了有意义的方程。

1　计算方法

采用半经验量子化学计算方法 MNDO 法计算了 18 种化合物的 E_{LUMO}、E_{HOMO}、$\Delta(\Delta H_f)$、μ 及 Q_{-NO_2}。MNDO 法可自动优化键长、键角，计算与热力学性质及反应途径有关的参数效果更好。计算中所用键长、键角取自文献[1－2]。

统计分析使用 Statgraphics 程序。

2　结果与讨论

5 种量化参数 E_{LUMO}、E_{HOMO}、$\Delta(\Delta H_f)$、μ 及 Q_{-NO_2}的数值列于表 1。

E_{LUMO}为分子最低空轨道能（eV），与分子对电子亲和力有关，其负值越大，表明电子进入该轨道后体系能量降低得越多，即该分子接受电子的能力越强[3]。表 1 的结果表明，$-E_{LUMO}$ 由高到低的顺序为：二硝基苯＞二硝基甲苯＞二硝基苯胺＞硝基氟苯＞硝基苯酚＞硝基苯甲醚＞硝基苯胺。

E_{HOMO}为分子最高占有轨道能（eV），与分子电离势有关，可作为分子给出电子能力的量度。$-E_{HOMO}$越小，分子越易给出电子被氧化[3]。本系列化合物的氧化趋势依次为：单硝基苯胺＞硝基苯酚≈硝基苯甲醚＞二硝基苯胺＞硝基甲苯＞二硝基甲苯＞二硝基苯。

$\Delta(\Delta H_f)$为化合物分子带一个负电荷（阴离子）的生成热与其中性分子的生成热之差（J/mol）。$\Delta(\Delta H_f)$值越低，化合物越容易得到一个电子而成为阴离子[4]。各化合物的 $\Delta(\Delta H_f)$与 E_{LUMO}所反映的趋势基本一致。

μ 为偶极矩，是表示极性分子电性质的参数[德拜(D)]。

Q_{-NO_2}为分子中最缺电子硝基的净电荷。对于系列硝基芳烃而言，其为负值，负得越多，表

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明该硝基上的电子密度越高，与亲核试剂的反应活性越弱[5]。

硝基芳烃对斜生栅列藻的毒性值以半数有效抑制浓度 EC_{50}(mol/L)表示，其实验方法及数据参见文献[6]，毒性值列于表1。

本文使用这5种量化参数，对斜生栅列藻的毒性进行统计分析，经过一元线性回归，得到如表2所示一系列方程。

表1 硝基芳烃的5种量子化学描述符及对斜生栅列藻的毒性

序号	化合物名称	$-E_{LUMO}$	$-E_{HOMO}$	$-\Delta(\Delta H_f)$	μ	$-Q_{-NO_2}$	实验毒性	计算毒性	残差
1	2-硝基甲苯	1.216	10.148	37.13	5.33	0.205	3.20	3.39	−0.19
2	4-硝基甲苯	1.263	10.301	39.59	5.52	0.197	3.74	3.55	0.19
3	1，2-二硝基苯	2.157	11.092	57.77	7.67	0.146	5.04	4.91	0.13
4	1，3-二硝基苯	2.087	11.217	58.73	5.00	0.168	4.85	4.72	0.13
5	1，4-二硝基苯	2.365	11.104	65.01	0.01	0.168	4.96	4.81	0.15
6	2，4-二硝基甲苯	2.096	11.059	59.93	5.49	0.167	4.52	4.90	−0.38
7	2，6-二硝基甲苯	2.000	10.990	51.65	3.72	0.182	4.06	4.13	−0.07
8	硝基苯	1.218	10.308	36.81	5.39	0.196	3.26	3.32	−0.06
9	2-硝基苯胺	0.942	9.096	31.80	5.44	0.223	3.33	3.28	0.05
10	3-硝基苯胺	1.031	9.022	34.78	6.40	0.204	3.48	3.61	−0.13
11	4-硝基苯胺	0.875	9.189	28.54	7.65	0.210	3.40	3.19	0.21
12	2，4-二硝基苯胺	1.662	9.983	48.93	7.32	0.183	4.68	4.51	0.17
13	2-硝基苯酚	1.153	9.768	36.22	6.50	0.181	3.51	3.52	−0.01
14	3-硝基苯酚	1.281	9.735	40.93	6.27	0.193	3.75	3.87	−0.12
15	4-硝基苯酚	1.205	9.886	37.88	5.64	0.199	3.57	3.54	0.03
16	2-硝基苯甲醚	1.077	9.612	35.10	6.42	0.186	3.44	3.47	−0.03
17	3-硝基苯甲醚	1.216	9.616	40.02	6.50	0.193	3.71	3.86	−0.15
18	4-硝基苯甲醚	1.146	9.753	36.88	6.21	0.201	3.65	3.55	0.10

表2 量化参数与毒性值 $-\log EC_{50}$ 的一元线性相关

参数	方程 $y=a+bx$		
	a	b	r
$\Delta(\Delta H_f)$	1.59	−0.053	0.932
E_{LUMO}	2.17	−1.20	0.917
Q_{-MO_2}	9.30	28.59	−0.850
E_{HOMO}	−2.17	−0.65	0.760
μ	4.49	−0.104	−0.288

从表2各方程的相关系数看，$\Delta(\Delta H_f)$与E_{LUMO}作为唯一变量描述藻类毒性得到较好结果，说明该系列中的大多数化合物的毒性作用与分子得电子被还原的能力有关。Q_{-NO_2}和E_{HOMO}与毒性也有一定的相关性，这表明某些硝基芳烃在藻体内可能通过亲核取代反应或氧化反应而致毒。μ与毒性的相关性很小。

若同时使用5个参数进行逐步回归分析，得到如下3参数方程：

$$-\log EC_{50} = 2.92 - 0.077\Delta(\Delta H_f) + 0.08\mu + 0.28E_{HOMO} \quad (1)$$

$$n = 18 \qquad r = 0.961 \qquad S = 0.173$$

式中，n为方程所含化合物数目，r为相关系数，S为标准偏差。表1列出了使用该方程对斜生栅列藻的毒性计算值和残差。需要说明的是，虽然$\Delta(\Delta H_f)$和E_{LUMO}均与毒性值有较好相关性，但由于这2个参数之间具有显著相关(相关系数0.99)，所以，2参数在逐步回归分析中不能同时出现在方程中。

从方程(1)的统计结果可以看出，联合使用$\Delta(\Delta H_f)$、μ和E_{EOMO}能更好的描述硝基芳烃对藻类的毒性。在方程(1)的逐步回归过程中，首先出现的参数是$\Delta(\Delta H_f)$，然后是μ，最后出现E_{HOMO}。由于$\Delta(\Delta H_f)$表示化合物分子得到电子被还原的能力，因此认为，在所研究的硝基芳烃中，还原反应是主要致毒因素，尤其那些$\Delta(\Delta H_f)$值低的二硝基苯、二硝基甲苯类。分子偶极矩在方程中出现，推测分子极性的作用可能与化合物到达受体的反应部位并与之结合的能

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COD 和 BOD_5 由于原水浓度超常的高导致超标外，其余的污染指标及各污染物 3 日平均浓度均符合上述国家排放标准。

(3) 表 3 表明，该工艺对硫化物、色度、COD 和 BOD_5 均具有很高的去除率、其中 S^{2-} 高达 100%，色度高达 99.2%，COD 高达 90.7%，BOD_5 高达 87.4%，其平均值分别为 97.0%、98.9%、87.4%和 85.7%。

表 3　新乡市环境保护监测站监测结果

取样日期	污染物	原水浓度 (mg/L)	出水浓度 (mg/L)	去除率 (%)
09-08	COD	324.1	30.19	90.68
	BOD_5	44.45	29.47	33.70
	S^{2-}	14.0	4.4	68.57
	SS	92	87	5.43
09-09	COD	3046	368.9	87.89
	BOD_5	1309.22	164.38	87.44
	S^{2-}	84.6	1.6	98.11
	SS	418	90	78.47
09-10	COD	543.8	93.59	82.79
	BOD_5	189.22	43.28	77.12
	S^{2-}	23.2	未检出	100
	SS	83	75	9.64
3 日平均值	COD	1304.6	164.2	87.41
	BOD_5	514.3	79.04	84.63
	S^{2-}	40.6	2.0	95.07
	SS	197.7	84	57.51

2.2　处理效益分析

采用本工艺处理 1 t 废水需电费 0.05 元、药剂费 0.30 元，人工费 0.08 元，总处理费用为 0.43 元/t。按设计 500 t/d 计，则年处理费用需 6.45 万元。

经处理后的废水，通过集水池可回用于设备冲洗、锅炉除尘和卫生用水，年回收水量 10 万 t，价值 4 万元，且可免交排污 15 万元/a，消除了高浓度硫化染色废水对环境的污染。

3　结论

混凝沉淀-铁屑过滤-碱析处理高浓度硫化染色废水组合工艺，集混凝、吸附、物化、电化、絮凝等综合作用于一体。其工艺流程合理、运行高效稳定、操作管理简便、工程投资和处理费用低廉。对硫化物、色度、COD 和 BOD_5 的总平均去除率分别高达 97.0%、98.9%、87.4%和 85.7%；处理后的水质各污染指标可以达到国家《污水综合排放标准》和《纺织染整工业水污染物排放标准》中的二级标准。适用于印染行业高浓度硫化染色废水的处理。

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力有关。E_{HOMO}在模式中最后出现，表明有些化合物在藻胞内发生了氧化反应，主要是那些$-E_{HOMO}$低的、易给出电子的胺类、酚类化合物。

3　结语

采用量子化学 MNDO 法计算了 18 种硝基芳烃的 5 种描述符 E_{LUMO}、E_{HOMO}、$\Delta(\Delta H_f)$、μ 及 Q_{-NO_2}。应用 5 参数对斜生栅列藻的急性毒性值进行了 QSAR 研究，得到有意义的方程，应用方程计算了所研究系列化合物的毒性。从对量化数据的分析和 QSAR 方程的研究，推测本系列化合物中，二硝基苯、二硝基甲苯的反应活性较高，在体内容易发生还原反应，产生毒性；硝基苯胺、二硝基苯胺及硝基苯酚类化合物在体内易于氧化；硝基苯、硝基甲苯、硝基苯甲醚等反应活性相对较弱。

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Study on the Catalytically Hydrogenated Conversion of CO_2 Using Ru/Al_2O_3 Catalyst. Zhao Ruilan et al. (Research Center for Eco-Environmental Sciences, Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 23—25

In this paper the catalytically hydrogenated conversion of CO_2 was studied using Ru/Al_2O_3 catalyst, the influence of different reaction conditions, such as reaction temperature (260—520℃, 5000—10000 h^{-1}) and CO_2/H_2 ratio in inlet gas, on CO_2 conversion efficiency and CH_4 formation were reported. At reaction temperature higher than 350℃ the CO_2 conversion efficiency was over 95%. and CH_4 formation rate was about 45%—79%. There was no significant influence on CO_2 conversion efficiency and H_2O formation when the space velocity from 5000 h^{-1} to 10000 h^{-1}. However, for the CH_4 formation efficiency there was a trough at the space velocity of 7000—9000 h^{-1}. The CO formation changed a little at space velocity of 5000—9000 h^{-1}, but it increased a lot at 10000 h^{-1}. The higher CH_4 formation efficiency was obtained when there existed excess of H_2. The highest CH_4 formation efficiency obtained was 98%.

Key words: carbon dioxide, catalyst, catalytically hydrogenated, methane.

Monitoring on The Concentration of Atmospheric Methane of A Rice Cropping Region in Beijing Area. Cui Ping et al. (Chinese Research Academy of Environmental Sciences, Beijing 100012): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 26—28

Monitoring on methane concentration in the atmosphere in the rice cropping region was carried out between Oct. 1991 and Nov. 1993. Results indicated that the average concentration of methane of the two testing years in the local region were 1.16 and 1.17 μg/L respectively. The variation of methane concentrations showed a strong seasonal pattern. The concentration and concentration deviation were high in summer and low in winter. During rice vegetation period, the methane concentrations were closely related with the variation of methane emission rates from rice paddies indicating rice paddies is one of the most important methane sources of the region. Running analysis showed that the average increasing rate of atmospheric methane in the region was 0.2%, much lower than some previous reports.

Key words: methane, rice, monitoring, Beijing area.

A simulation Study on the Accumulation of Added Rare Earth Elements in Aquatic Ecosystem. Chen Zhaoxi et al. (Dept. of Chem. Eng., East China Institute of Metallurgy, Maanshan 243002): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 29—31

The accumulation and distribution coefficients of added rare earth elements (RE) in various parts of simulated aquatic ecosystem were investigated. The results showed that concentrations of added RE in bottom mud and water bodies varied smoothly and in *Lemna minor* and *Cyprinus carpio* varied extremely with the time in the period of experiment. Distribution coefficients of added RE in bottom mud were higher than 96%, in *Lemna minnor*, were range of 0.26—1.61%, in water, were range of 0.54%—0.91%; and in carp were less than 0.035%, but almost on linear increment in the period of experiment. Bioconcentration of added RE in carp was also discussed.

Key words: aquatic ecosystem, accumulation, rare earth elements, bioconcentation.

The Quantum Chemistry Studies of the biradical Mechanism of Destroying Ozone in the Atmosphere. Sun Huabin et al. (Institute of Military Medicine, Jinan Command, Jinan 250014): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 32—34

The reaction mechanisms of the singlet biradicals NH, CH_2, CCl_2 with ozone in the atmosphere have been studied using RHF method of quantum chemistry. The geometries of the reactants, intermediates and products of the above reactions are optimized with the gradient technique at the 3-21G level, their energies have been calculated at the 6-31G or 6-21G level. The structure data of all species have been obtained. The calculated results show that there are two stages in the above reactions, the reactions of the biradicals with ozone take place first to form the stable intermediates, then the intermediates are decomposed by illuminating to the stable molecules HNO, H_2CO and Cl_2CO etc., respectively. In terms of dynamics two reactions in two stages belong to the types $[\pi_{4s}+W_{2s}]$ and $[\pi_{2s}+\pi_{2s}]$, respectively, and they are permited thermodynamically. In this study, a method to investigate complicated reaction based on the combining thermodynamics with Woodward-Hoffmann approach without calculation of transition state was attempted to provide by authors.

Key words: biradical, loss of ozone, reaction mechanism.

The Structure and Toxicity Relationship Study for Nitroaromatics to *Scenedesmus obliquus*. Lu Guanghua et al. (Dept. of Environ. Sci., Northeast Normal Univ., Changchun 130024): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 35—36

E_{LUMO}, E_{HOMO}, $\Delta(\Delta H_f)$, μ and $Q_{\cdot NO_2}$ of 18 nitroaromatic compounds were calculated using the quantum chemical method MNDO. The quantitative structure-activity relationships (QSAR) were developed using the five quantum chemical descriptors for the acute toxicity of nitroaromatics to *Scenedesmus obliquus*. Through step-wise regression analysis, one best equation contained three variables was obtained: $-\log EC_{50}=2.92-0.077\Delta(\Delta H_f)+0.08\mu+0.28E_{HOMO}$, $n=18$, $r=0.961$, $S=0.173$. The equaiton was used to estimate the toxicity of the studied compounds, and the toxic effect was discussed.

Key words: structure, toxicity, nitroaromatics, *Scenedesmus obliquus*.

Effects of Rare-Earth Elements on Growth and Reproduction of *Chlorella pyrenoides*. Hu Qinhai et al. (Dept. of Environ. Sci., Zhejiang Agricultural University, Hangzhou 310029): *Chin. J. Environ. Sci.*, **17**(2), 1996, pp. 37—38

It was studied that effects of rare-earth elements (La, Ce, Pr, Nd and their mixture) on growth and reproduction of *Chlorella pyrenoides*. The results showed that effects of rare-earth elements on growth and reproduction of *Chlorella pyrenoides* were not apparent under lower concentration (2 mg/L), but it was inhibited as the concen-