

• 研究论文 •

## 芳香胺类化合物 N—H 键离解能的定量构效关系研究

乔 澍 谢 昆 付 川 祁俊生\*

(重庆三峡学院化学与环境工程学院 重庆 404000)

**摘要** 基于启发式方法(HM)和 BP 神经网络方法建立了 5 个参数的定量结构性质关系(QSPR)模型,用于预测 80 个芳香胺类化合物 N—H 键的键离解能(BDE). 通过两种方法分别建立了线性和非线性的 QSPR 模型,相关系数  $R$  分别为 0.823 和 0.976. 通过对模型的稳定性和预测能力进行比较,发现 BP 神经网络方法能够更好地预测芳香胺类化合物 N—H 键的 BDE 值.

**关键词** 启发式方法; BP 神经网络; 定量结构性质关系; 键裂解能

## Quantitative Structure-property Relationship Study on N—H Bond Dissociation Energy of Arylamines

Qiao, Shu Xie, Kun Fu, Chuan Qi, Junsheng\*

(College of Chemistry & Environmental Engineering, Chongqing Three Gorges University, Chongqing 404000)

**Abstract** The bond dissociation energy (BDE) of 80 diverse arylamines was modeled using the five descriptors calculated from the molecular structure along with a quantitative structure-property relationship (QSPR) technique. The heuristic method (HM) and back-propagation neural network method were utilized to construct the linear and nonlinear prediction models, leading to the correlation coefficients  $R$  of 0.823 and 0.976. By comparison of the stability with prediction ability of the models, it was found that BP network was a good method for predicting the N—H BDE values of arylamines.

**Keywords** heuristic method; BP artificial neural network; quantitative structure-property relationship (QSPR); bond dissociation energy (BDE)

芳香胺类化合物由于具有一定的还原性质,常被作为抗氧化剂使用. 这类化合物中的 N—H 键离解能(bond dissociation energy 简写成 BDE)是影响化学键活性的一个重要因素,实验通过动力学方法、光致电离质谱分析技术和酸性/电子亲和性循环方法测定化合物在气相的键解离能<sup>[1]</sup>. 但是由于实验方法本身的缺陷及自由基寿命较短等原因导致实验测定某些化合物的键解离能时仍存在一定的困难. 目前利用高水平的量子化学从头计算方法可以获得多种化合物的键解离能<sup>[2~5]</sup>,但这种方法

要寻找一种经济方便并且能够精确预测大范围化合物 BDE 值的方法.

物质定量结构-性质/活性关系(QSPR/QSAR)在近年来发展很快,并且在预测和评估实际物质的活性和性质方面有着较为广泛的应用<sup>[6~10]</sup>. 本文创新性地使用 QSPR 方法来预测一系列结构复杂的芳香胺类化合物 N—H 键的 BDE 值,通过基于回归分析的启发式方法(HM)以及基于神经网络的反向传播(BP)网络方法对 80 种芳香胺类化合物进行建模,结果表明 BP 神经网络方法可以作为一种新的工具研究和预测化合物

\* E-mail: sanxiauqi@163.com; Tel.: 023-58960027

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的 BDE 值.

## 1 研究方法

### 1.1 数据的准备

本文中选取了 80 个芳香胺类化合物, 包括苯胺、苯肼、萘胺、二苯胺等(结构见表 1), 其 N—H 键 BDE 实验值全部摘自文献[11]. 随机选取其中的 60 个化合物作

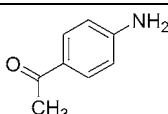
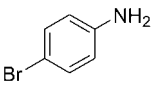
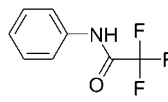
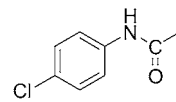
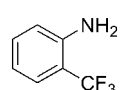
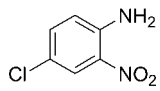
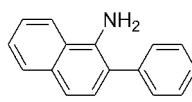
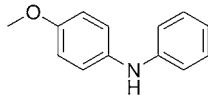
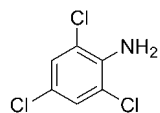
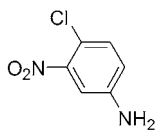
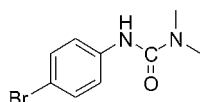
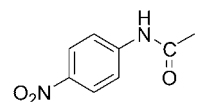
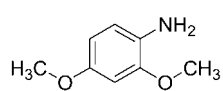
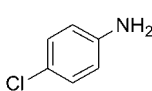
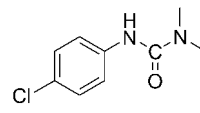
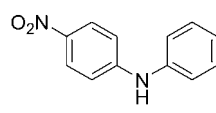
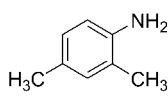
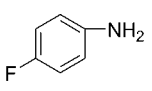
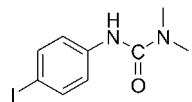
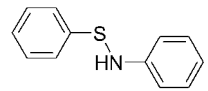
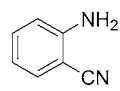
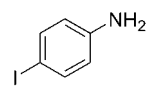
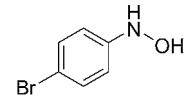
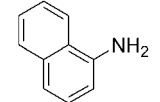
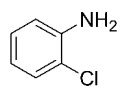
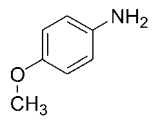
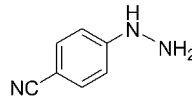
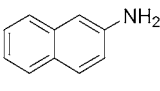
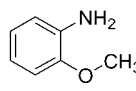
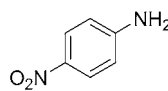
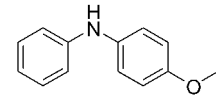
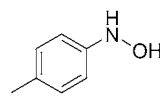
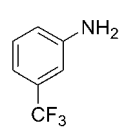
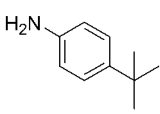
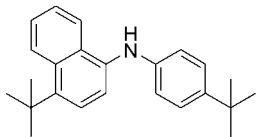
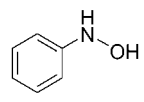
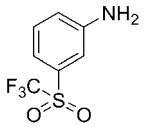
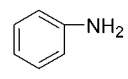
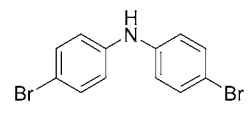
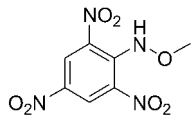
为训练集, 用于建立模型, 其余 20 个化合物作为测试集对模型的稳定性和预测能力进行检验.

使用 Hyperchem 画出所有 80 个化合物的结构并在该程序下进行 AM1 半经验几何优化, 将优化好的分子导入 MOPAC 计算软件中进行计算.

### 1.2 描述符的计算

将 MOPAC 的输出结果文件转入 CODESSA 程序中,

表 1 80 个样本化合物的结构及编号  
Table 1 Structures and numbers of 80 compounds

| No. | Structure   | No. | Structure   | No. | Structure  | No. | Structure   |
|-----|---|-----|---|-----|--|-----|---|
| 1   |    | 21  |    | 41  |    | 61  |    |
| 2   |    | 22  |    | 42  |    | 62  |    |
| 3   |   | 23  |   | 43  |   | 63  |   |
| 4   |  | 24  |  | 44  |  | 64  |  |
| 5   |  | 25  |  | 45  |  | 65  |  |
| 6   |  | 26  |  | 46  |  | 66  |  |
| 7   |  | 27  |  | 47  |  | 67  |  |
| 8   |  | 28  |  | 48  |  | 68  |  |
| 9   |  | 29  |  | 49  |  | 69  |  |
| 10  |  | 30  |  | 50  |  | 70  |  |

续表

| No. | Structure | No. | Structure | No. | Structure | No. | Structure |
|-----|-----------|-----|-----------|-----|-----------|-----|-----------|
| 11  |           | 31  |           | 51  |           | 71  |           |
| 12  |           | 32  |           | 52  |           | 72  |           |
| 13  |           | 33  |           | 53  |           | 73  |           |
| 14  |           | 34  |           | 54  |           | 74  |           |
| 15  |           | 35  |           | 55  |           | 75  |           |
| 16  |           | 36  |           | 56  |           | 76  |           |
| 17  |           | 37  |           | 57  |           | 77  |           |
| 18  |           | 38  |           | 58  |           | 78  |           |
| 19  |           | 39  |           | 59  |           | 79  |           |
| 20  |           | 40  |           | 60  |           | 80  |           |

即可计算化合物的五类分子描述符: 组成描述符(如分子中各类原子和化学键的种类、环的数量以及分子量等); 拓扑描述符(如 Wiener 指数、Kier-Hall 指数等); 几何描述符(如分子体积、分子表面积等); 静电描述符(如最大或最小局部电荷等)和量子描述符(偶极矩、HOMO

以及 LOMO 的能量等).

### 1.3 启发式回归方法

CODESSA 软件中的启发式方法(HM, Heuristic Method)<sup>[12]</sup>, 可对大量的分子描述符进行完全搜索, 从

而建立最佳的线性回归模型. 该方法的特点是对数据集大小没有限制, 计算速度很快, 并且可以同时得到几个最好的模型. 启发式方法在程序计算过程中并不是把所有的描述符列举并计算, 而是通过测试共线性(例如任意两个相关系数在 0.8 以上的参数不能出现在同一个模型中), 来减少运算量, 从而快速地建立并输出模型.

#### 1.4 BP 神经网络方法

BP (Back-Propagation) 神经网络又称误差反向传播训练算法, 是学者 Rumelhart 等<sup>[13]</sup>提出用以解决多层网络中隐含单元连接权的学习问题. 本文中使用了三层 BP 网络, 以启发式回归模型中最好的五参数模型中的五个描述符作为该 BP 网络的输入, 以 80 个芳香胺类化合物 N—H 键 BDE 的值作为输出, 建立神经网络模型.

## 2 结果讨论

### 2.1 启发式回归模型

通过启发式方法(HM)建立了 5 个参数的线性回归模型, 见表 2. HA dependent HDCA-2 [Zefirov's PC] 属于静电描述符, 表示由氢受体决定的氢给体电荷表面积. 其余 4 个参数均为量子描述符, min n-n repulsion for a H

—N bond 表示 H—N 键上原子核之间的排斥作用, min ( $>0.1$ ) bond order of a N atom 表示 N 原子的最小键级, tot point-charge comp. of the molecular dipole 表示构成分子偶极矩的总点电荷, min exchange energy for a H—N bond 表示 H—N 键的最小交换能. 这些参数都与 N—H 键密切相关.

HM 方法得到 N—H 键 BDE 的计算值与实验值之间相互关系参见图 1, 预测结果列于表 3. 训练集、测试集和整个数据集的 RMS 分别为 2.17, 6.15 和 4.45; 相应的相关系数  $R$  分别为 0.877, 0.659 和 0.823.

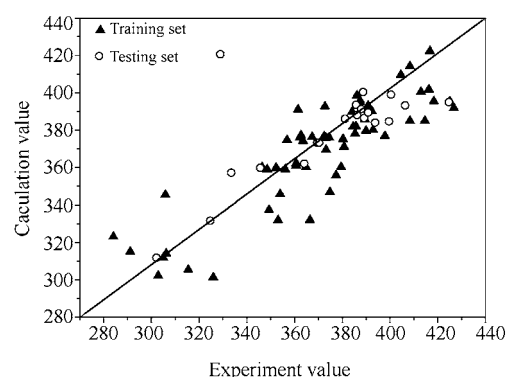


图 1 HM 方法得到 N—H 键 BDE 预测值 vs. 实验值  
Figure 1 Plot of predicted N—H BDE versus experimental values based on the HM method

表 2 含 5 个参数的多元线性模型<sup>a</sup>

Table 2 Multilinear model contains 5 descriptors

| Descriptor                                     | Coefficient | SD     | Beta   | <i>t</i> -Test |
|--|-------------|--------|--------|----------------|
| intercept                                      | -643.621    | 75.599 | —      | -8.514         |
| min n-n repulsion for a H—N bond               | 11.407      | 1.731  | 0.550  | 6.590          |
| min ( $>0.1$ ) bond order of a N atom          | -19.308     | 2.371  | -0.716 | -8.143         |
| HA dependent HDCA-2 [Zefirov's PC]             | -263.963    | 57.271 | -0.359 | -4.609         |
| tot point-charge comp. of the molecular dipole | 0.644       | 0.258  | 0.165  | 2.500          |
| min exchange energy for a H—N bond             | 24.179      | 8.196  | 0.281  | 2.950          |

<sup>a</sup>  $R^2=0.7037$ ;  $s=4.48$ ;  $F=33.26$ ;  $n=80$ .

表 3 HM 和 BP 方法得到的 N—H 键 BDE 值

Table 3 Predicted N—H BDE values by HM and BP methods

| No | Compound name                          | Exp./ $(\text{kJ}\cdot\text{mol}^{-1})$ | HM/ $(\text{kJ}\cdot\text{mol}^{-1})$ | Error/ $(\text{kJ}\cdot\text{mol}^{-1})$ | ANN/ $(\text{kJ}\cdot\text{mol}^{-1})$ | Error/ $(\text{kJ}\cdot\text{mol}^{-1})$ |
|----|--|---|---------------------------------------|--|--|--|
| 1  | 1-(4-Aminophenyl)ethanone              | 381.16                                  | 386.06                                | 4.90                                     | 384.59                                 | 3.43                                     |
| 2  | 2-(Trifluoromethyl)benzenamine         | 389.11                                  | 386.48                                | -2.64                                    | 386.43                                 | -2.68                                    |
| 3  | 2,4,6-Trichlorobenzenamine             | 399.57                                  | 384.64                                | -14.94                                   | 386.27                                 | -13.31                                   |
| 4  | 2,4-Dimethoxybenzenamine               | 369.45                                  | 373.25                                | 3.81                                     | 363.51                                 | -5.94                                    |
| 5  | 2,4-Dimethylbenzenamine                | 370.28                                  | 373.34                                | 3.05                                     | 373.80                                 | 3.51                                     |
| 6  | 2-Aminobenzonitrile                    | 397.90                                  | 376.89                                | -21.00                                   | 399.40                                 | 1.51                                     |
| 7  | 2-Chlorobenzenamine                    | 389.53                                  | 385.68                                | -3.85                                    | 376.27                                 | -13.31                                   |
| 8  | 2-Methoxybenzenamine                   | 373.21                                  | 369.49                                | -3.72                                    | 368.95                                 | -4.27                                    |
| 9  | 3-(Trifluoromethyl)benzenamine         | 392.46                                  | 389.95                                | -2.51                                    | 380.12                                 | -12.34                                   |
| 10 | 3-(Trifluoromethylsulfonyl)benzenamine | 400.41                                  | 399.03                                | -1.38                                    | 398.53                                 | -1.88                                    |

续表

| No | Compound name  | Exp./( $\text{kJ}\cdot\text{mol}^{-1}$ ) | HM/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Error/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | ANN/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Error/( $\text{kJ}\cdot\text{mol}^{-1}$ ) |
|----|--|--|--|---|---|---|
| 11 | 3,4-Dimethoxybenzenamine   | 372.38                                   | 376.56                                 | 4.18                                      | 375.05                                  | 2.68                                      |
| 12 | 3,4-Dimethylbenzenamine  | 373.21                                   | 375.85                                 | 2.64                                      | 374.47                                  | 1.26                                      |
| 13 | 3,5-Dimethoxybenzenamine   | 385.35                                   | 378.11                                 | -7.24                                     | 384.51                                  | -0.84                                     |
| 14 | 3,5-Dimethylbenzenamine  | 380.33                                   | 375.14                                 | -5.19                                     | 374.30                                  | -6.02                                     |
| 15 | 3-Aminobenzonitrile  | 393.71                                   | 384.01                                 | -9.71                                     | 392.54                                  | -1.17                                     |
| 16 | 3-Bromobenzenamine   | 389.95                                   | 379.61                                 | -10.33                                    | 382.42                                  | -7.53                                     |
| 17 | 3-Chlorobenzenamine  | 387.44                                   | 395.72                                 | 8.28                                      | 385.89                                  | -1.55                                     |
| 18 | 3-Methoxybenzenamine   | 392.88                                   | 380.12                                 | -12.76                                    | 382.92                                  | -9.96                                     |
| 19 | 4-(Trifluoromethyl)benzenamine   | 387.44                                   | 395.01                                 | 7.57                                      | 386.35                                  | -1.09                                     |
| 20 | 4-Aminobenzonitrile  | 386.18                                   | 388.11                                 | 1.92                                      | 389.49                                  | 3.31                                      |
| 21 | 4-Bromobenzenamine   | 385.76                                   | 381.96                                 | -3.81                                     | 387.06                                  | 1.30                                      |
| 22 | 4-Chloro-2-nitrobenzenamine  | 408.36                                   | 384.97                                 | -23.39                                    | 402.88                                  | -5.48                                     |
| 23 | 4-Chloro-3-nitrobenzenamine  | 408.36                                   | 414.17                                 | 5.82                                      | 408.02                                  | -0.33                                     |
| 24 | 4-Chlorobenzenamine  | 386.18                                   | 398.57                                 | 12.38                                     | 390.16                                  | 3.97                                      |
| 25 | 4-Fluorobenzenamine  | 388.69                                   | 400.37                                 | 11.67                                     | 389.82                                  | 1.13                                      |
| 26 | 4-Iodobenzenamine  | 372.79                                   | 392.58                                 | 19.79                                     | 386.43                                  | 13.64                                     |
| 27 | 4-Methoxybenzenamine   | 367.36                                   | 376.27                                 | 8.91                                      | 372.54                                  | 5.19                                      |
| 28 | 4-Nitrobenzenamine   | 404.59                                   | 409.57                                 | 4.98                                      | 407.10                                  | 2.51                                      |
| 29 | 4- <i>tert</i> -Butylbenzenamine   | 374.47                                   | 376.02                                 | 1.55                                      | 376.02                                  | 1.55                                      |
| 30 | Aniline  | 385.76                                   | 393.55                                 | 7.78                                      | 379.61                                  | -6.15                                     |
| 31 | Benzene-1,4-diamine  | 362.33                                   | 376.14                                 | 13.81                                     | 360.54                                  | -1.80                                     |
| 32 | <i>o</i> -Toluidine  | 361.50                                   | 390.99                                 | 29.50                                     | 380.33                                  | 18.83                                     |
| 33 | <i>p</i> -Toluidine  | 384.51                                   | 381.92                                 | -2.59                                     | 384.84                                  | 0.33                                      |
| 34 | 1-(4-Chlorophenyl)hydrazine  | 306.27                                   | 314.18                                 | 7.91                                      | 307.15                                  | 0.88                                      |
| 35 | 1,1-Dimethyl-3-phenylurea  | 387.86                                   | 391.29                                 | 3.43                                      | 380.41                                  | -7.45                                     |
| 36 | 1,1-Dimethyl-3- <i>p</i> -tolylurea  | 384.09                                   | 389.82                                 | 5.73                                      | 386.10                                  | 2.01                                      |
| 37 | 1,2-Diphenylhydrazine  | 305.85                                   | 345.39                                 | 39.54                                     | 315.14                                  | 9.29                                      |
| 38 | 1-Phenylhydrazine  | 305.01                                   | 311.88                                 | 6.86                                      | 305.72                                  | 0.71                                      |
| 39 | 1-Phenylnaphthalen-2-amine   | 362.75                                   | 377.23                                 | 14.48                                     | 371.00                                  | 8.24                                      |
| 40 | 1- <i>p</i> -Tolylhydrazine  | 302.08                                   | 311.88                                 | 9.79                                      | 306.85                                  | 4.77                                      |
| 41 | 2,2,2-Trifluoro- <i>N</i> -phenyl-acetamide  | 416.73                                   | 422.33                                 | 5.61                                      | 416.06                                  | -0.67                                     |
| 42 | 2-Phenylnaphthalen-1-amine   | 356.90                                   | 374.72                                 | 17.82                                     | 366.94                                  | 10.04                                     |
| 43 | 3-(4-Bromophenyl)-1,1-dimethylurea   | 391.20                                   | 391.87                                 | 0.67                                      | 389.07                                  | -2.13                                     |
| 44 | 3-(4-Chlorophenyl)-1,1-dimethylurea  | 390.79                                   | 393.04                                 | 2.26                                      | 387.65                                  | -3.14                                     |
| 45 | 3-(4-Iodophenyl)-1,1-dimethylurea  | 390.79                                   | 389.45                                 | -1.34                                     | 392.25                                  | 1.46                                      |
| 46 | 4-Bromo- <i>N</i> -hydroxybenzenamine  | 302.92                                   | 302.25                                 | -0.67                                     | 304.60                                  | 1.67                                      |
| 47 | 4-Hydrazinylbenzonitrile   | 325.93                                   | 301.46                                 | -24.48                                    | 327.77                                  | 1.84                                      |
| 48 | 4-Methoxy- <i>N</i> -phenylbenzenamine   | 356.06                                   | 359.03                                 | 2.97                                      | 353.59                                  | -2.47                                     |
| 49 | 4- <i>tert</i> -Butyl- <i>N</i> -(4- <i>tert</i> -butylphenyl)-naphthalen-1-amine        | 352.29                                   | 359.82                                 | 7.53                                      | 350.83                                  | -1.46                                     |
| 50 | Bis(4-bromophenyl)amine  | 364.01                                   | 362.08                                 | -1.92                                     | 365.35                                  | 1.34                                      |
| 51 | Bis(4-methoxyphenyl)amine  | 348.53                                   | 359.11                                 | 10.59                                     | 349.36                                  | 0.84                                      |
| 52 | Bi(naphthalen-2-yl)amine   | 360.66                                   | 362.25                                 | 1.59                                      | 365.72                                  | 5.06                                      |
| 53 | Diphenylamine  | 364.84                                   | 360.16                                 | -4.69                                     | 360.83                                  | -4.02                                     |
| 54 | Dip-tolylamine   | 360.66                                   | 360.91                                 | 0.25                                      | 361.12                                  | 0.46                                      |
| 55 | <i>N</i> <sup>1</sup> , <i>N</i> <sup>4</sup> -Bis(4-isopropylphenyl)benzene-1,4-diamine | 333.46                                   | 357.23                                 | 23.77                                     | 336.73                                  | 3.26                                      |
| 57 | <i>N</i> -(4-(Trifluoromethyl)phenyl)acetamide   | 346.44                                   | 360.20                                 | 13.77                                     | 353.88                                  | 7.45                                      |

续表

| No | Compound name                               | Exp./( $\text{kJ}\cdot\text{mol}^{-1}$ ) | HM/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Error/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | ANN/( $\text{kJ}\cdot\text{mol}^{-1}$ ) | Error/( $\text{kJ}\cdot\text{mol}^{-1}$ ) |
|----|---|--|--|---|---|---|
| 58 | <i>N</i> -(4-Acetylphenyl)acetamide         | 418.40                                   | 395.43                                 | -22.97                                    | 419.70                                  | 1.30                                      |
| 59 | <i>N</i> -(4-Bromophenyl)acetamide          | 414.63                                   | 384.93                                 | -29.71                                    | 404.93                                  | -9.71                                     |
| 60 | <i>N</i> -(4-Cyanophenyl)acetamide          | 424.68                                   | 395.01                                 | -29.66                                    | 421.16                                  | -3.51                                     |
| 61 | <i>N</i> -(4-Chlorophenyl)acetamide         | 412.96                                   | 400.45                                 | -12.51                                    | 411.37                                  | -1.59                                     |
| 62 | <i>N</i> -(4-Methoxyphenyl)benzenamine      | 353.13                                   | 331.96                                 | -21.17                                    | 357.19                                  | 4.06                                      |
| 63 | <i>N</i> -(4-Nitrophenyl)acetamide          | 426.77                                   | 391.79                                 | -34.98                                    | 423.76                                  | -3.01                                     |
| 64 | <i>N</i> -(4-Nitrophenyl)benzenamine        | 380.74                                   | 371.08                                 | -9.67                                     | 383.38                                  | 2.64                                      |
| 65 | <i>N</i> -(Phenylthio)benzenamine           | 345.60                                   | 359.82                                 | 14.23                                     | 352.29                                  | 6.69                                      |
| 66 | Naphthalen-1-amine                          | 374.89                                   | 346.81                                 | -28.07                                    | 373.67                                  | -1.21                                     |
| 67 | Naphthalen-2-amine                          | 379.49                                   | 360.16                                 | -19.33                                    | 363.51                                  | -15.98                                    |
| 68 | <i>N</i> -Hydroxy-4-methylbenzenamine       | 284.09                                   | 323.13                                 | 39.04                                     | 296.52                                  | 12.43                                     |
| 69 | <i>N</i> -Hydroxybenzenamine                | 291.21                                   | 315.10                                 | 23.89                                     | 289.07                                  | -2.13                                     |
| 70 | <i>N</i> -Methoxy-2,4,6-trinitrobenzenamine | 324.68                                   | 331.67                                 | 6.99                                      | 325.93                                  | 1.26                                      |
| 71 | <i>N</i> -Methoxy-2,6-dinitrobenzenamine    | 315.47                                   | 305.47                                 | -10.00                                    | 318.44                                  | 2.97                                      |
| 72 | <i>N</i> - <i>m</i> -Tolylbenzenamine       | 366.52                                   | 332.08                                 | -34.43                                    | 346.56                                  | -19.96                                    |
| 73 | <i>N</i> -Phenoxy-naphthalen-2-amine        | 349.36                                   | 337.44                                 | -11.92                                    | 350.49                                  | 1.13                                      |
| 74 | <i>N</i> -Phenylacetamide                   | 416.31                                   | 401.75                                 | -14.56                                    | 413.88                                  | -2.43                                     |
| 75 | <i>N</i> '-Phenylacetohydrazide             | 328.86                                   | 420.62                                 | 91.76                                     | 345.39                                  | 16.53                                     |
| 76 | <i>N</i> -Phenylbenzothioamide              | 377.40                                   | 355.77                                 | -21.63                                    | 359.32                                  | -18.07                                    |
| 77 | <i>N</i> -Phenyl-naphthalen-1-amine         | 352.29                                   | 359.78                                 | 7.49                                      | 358.78                                  | 6.49                                      |
| 78 | <i>N</i> -Phenyl-naphthalen-2-amine         | 353.97                                   | 345.72                                 | -8.24                                     | 359.91                                  | 5.94                                      |
| 79 | <i>N</i> - <i>p</i> -Tolylbenzenamine       | 363.59                                   | 374.18                                 | 10.59                                     | 377.31                                  | 13.72                                     |
| 80 | <i>N</i> - <i>p</i> -Tolylacetamide         | 406.27                                   | 393.25                                 | -13.01                                    | 387.44                                  | -18.83                                    |

从以上图表可以看出, HM 方法所建立线性模型的预测结果并不令人满意, 但是模型中的 5 个参数对于芳香胺化合物 N—H 键 BDE 值的影响显著.

## 2.2 BP 人工神经网络模型

相同的描述符作为 BP 神经网络的输入, N—H 键 BDE 的实验值作为输出建立非线性模型, 进一步讨论芳香胺类分子结构与 N—H 键 BDE 间的关系.

BP 网络的隐含层节点数为 4, 得到的结果见表 3 和图 2. 训练集、测试集和整个数据集的 *RMS* 分别为 0.874, 2.03 和 0.845; 相应的相关系数 *R* 分别为 0.978, 0.970 和 0.976. 通过比较可以看出, BP 神经网络的预测结果优于 HM 方法.

## 2.3 Hammett 常数与 N—H 键 BDE 的关系

Bosque 等<sup>[14]</sup>曾使用 QSPR 方法对苯酚类化合物的 O—H 键裂解能进行预测, 以 Hammett 常数为参数建立了线性模型. 为了进行比较, 我们选择了 80 个芳香胺化合物中 17 个一取代苯胺化合物, 建立了其 N—H 键 BDE 与取代基 Hammett 常数间的相关模型, 见图 3. 模型的相关系数  $R=0.80$ , 表明取代基的 Hammett 常数与苯胺类化合物的 N—H 键 BDE 值之间确实存在定量关系. 但是

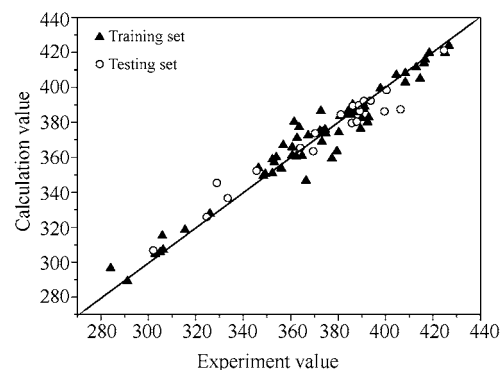


图 2 BP 方法得到 N—H 键 BDE 预测值 vs. 实验值  
Figure 2 Plot of predicted N—H BDE versus experimental values based on the BP neural networks

此模型的预测结果比起 BP 神经网络的结果稍逊一筹.

## 3 结论

本文首次提出了基于 HM 和 BP 人工神经网络方法预测芳香胺类化合物的键解离能(BDE), 并建立了线性、非线性的 QSPR 模型, 开辟了预测化合物 BDE 的新思路. 比较两种方法, 结果表明非线性的 BP 人工神经

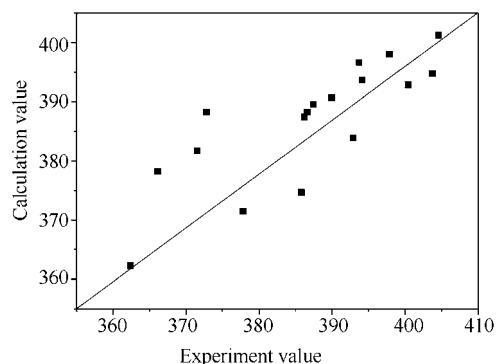


图3 基于 Hammett 常数的 N—H 键 BDE 预测值 vs. 实验值  
Figure 3 Plot of predicted N—H BDE versus experimental values based on the Hammett constants

网络方法明显优于 HM 方法, 可以作为一种新的研究和预测 BDE 值的有利工具.

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