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用分子子图法计算硝基呋咱化合物的生成热

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摘 要： 用新的分子子图法计算硝基呋咱类化合物的生成热，将呋咱基团视为母体，即基子图项 硝基、叠氮基、甲基、氰基拆分为一个个原子，从原子的角度来分分子子图，将碳、氢、氧、氮原子视为取代基，即亚子图项.同时考虑呋咱基团的个数，考虑 1 位、2 位、3 位、4 位上碳、氢、氧、氮原子及双键、叁键对生成热的影响，还考虑不饱和度、总硝基个数、环的个数（除呋咱环）、氮氮及氮氧双键的个数对生成热的影响.用这种新的分子子图编码方法，对硝基呋咱化合物的生成热进行了拟合和预估，取得了满意的结果，其回归方程的相关系数达到了 0.9954.

关键词： 分子子图；QSPR；硝基呋咱；生成热
中图分类号：O621.2 **文献标识码：**A

1 引 言

生成热（又称焓）是重要的热力学函数，是化学计算与工程设计中常用到的基础数据，它对评定含能材料或火炸药能量水平有重要意义，根据化合物的生成热可计算出推进剂的比冲、特征速度、燃烧温度等能量特征参数[1]，也可计算出炸药的爆压、爆速等爆轰参数，呋咱类多硝基化合物是一类新型化合物，它们的生成热数据报道得较少，我们根据文献的部分数据[2]，从拓扑学角度研究定量构造关系（QSPR），进行了拟合建模[3-7]，达到较好的效果，依此方法，可以预估新的硝基呋咱的生成热，为新的高能化合物的设计打下基础.

2 编码原理与方法

硝基呋咱基团是一个环状的强共轭体系，在分解含呋咱基团化合物的子图时，不能将呋咱基团分解，故把硝基呋咱基团或呋咱基团看作一个整体，视为母体，即基子图项，将氮原子、氧原子、碳原子、氢原子视为取代基，即亚子图项.

分子是一个非数值的数学对象，其各种可测量的性质通常又都是用数值表达的.因此，为了把分子的拓扑性质与其各种可测量的性质联系起来，必须把在分子子图中获得的信息转变为一种能用数值表达的量[1].在硝基呋咱类化合物中，我们以呋咱基团为母体，考虑呋咱基团的个数、考虑 1 位 N、O、C，2 位 N、O、H，3 位 N、O，4 位 N、O 原子对其生成热的影响，还考虑 1 位、2 位、3 位双键以及三键的不同个数的影响，再考虑不饱和度、总硝基个数、环的个数（除呋咱环）、氮氮双键的个数、氮氧双键的个数对生成热的影响.以图 1（a）所示的化合物为例，对于左边的呋咱基团，编码方法可见图 1（b）；对于右边的呋咱基团编码方法，可见图 1（c）.以此方法，我们得到呋咱系列化合物的子图编码表（表 1）.

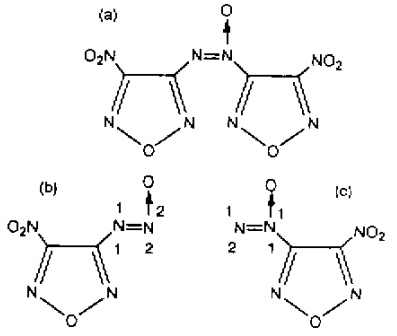

图 1 硝基呋咱化合物及其编码方法示意图

Fig.1 Illustration for coding nitro furazan compound

3 结果与讨论

3.1 回归方程建立

用以上子图编码对生成热的数值进行多元线性回归，对 31 组数据进行回归，其回归方程的相关系数达 0.9954.可见，用分子子图编码方法建立的模拟计算公式和方法是可靠和有效的.回归方程为：

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表 1 呋咱系列化合物的子图编码表

Table 1 Coding of furazan series compounds

No.	B	1N	1O	1C	2N	2O	3N	3O	4O	4N	2H	1DB	2DB	3DB	TB	Ust.	No. NO_2	R	N=N	N=O	ΔH_f/(kJ/mol)
2	1	2	0	0	1	2	1	0	0	0	0	3	0	0	1	5	1	0	1	0	530.48
3	1	1	1	0	0	2	0	0	0	0	1	2	0	0	0	2	1	0	0	0	261.92
4	1	2	0	0	1	2	0	2	0	0	1	4	0	0	0	4	2	0	0	0	498.83
5	1	1	0	1	1	2	0	0	0	0	0	2	0	0	1	4	1	0	0	0	208.33
6	1	1	0	1	3	2	0	6	0	0	0	2	6	0	0	8	4	0	0	0	292.60
7	1	1	0	1	3	2	1	4	0	1	0	2	5	0	1	9	3	0	1	0	608.86
8	1	1	0	1	0	3	1	0	0	0	2	2	0	2	0	4	2	0	0	0	43.26
9	1	1	0	1	1	2	1	0	0	1	2	2	1	0	1	5	1	0	1	0	395.05
10	1	1	0	1	0	2	0	0	0	0	3	2	0	0	0	2	1	0	0	0	171.05
12	2	2	0	0	0	4	0	0	0	0	0	4	0	0	0	4	2	0	0	0	352.00
13	2	2	2	0	0	4	0	0	0	0	0	4	0	0	0	4	2	0	0	0	294.36
15	2	4	0	0	2	5	0	1	0	0	0	7	1	0	0	6	2	0	1	1	620.35
16	2	4	0	0	2	4	0	4	0	0	0	4	4	0	0	6	3	0	0	0	367.38
17	2	4	0	0	0	4	0	0	0	0	1	4	0	0	0	4	2	0	0	0	487.05
20	2	2	0	2	0	6	0	0	0	0	0	6	0	0	0	5	2	0	0	0	445.25
21	2	2	1	1	0	6	0	1	0	0	0	5	1	0	0	5	2	0	0	0	327.04
22	2	2	0	2	4	4	0	8	0	0	0	4	8	0	0	8	4	0	0	0	328.42
24	2	2	0	2	2	4	2	0	4	0	4	4	0	4	0	6	3	0	0	0	397.73
25	3	2	4	0	0	4	0	0	0	0	0	4	0	0	0	4	2	0	0	0	415.99
26	3	6	0	0	4	4	0	0	0	0	0	8	0	0	0	6	2	0	2	0	1227.83
27	3	6	0	0	4	6	0	2	0	0	0	10	2	0	0	8	2	0	2	2	1098.84
31	4	4	4	0	2	5	0	1	0	0	0	7	1	0	0	6	2	0	1	1	813.80
34	4	8	0	0	6	4	0	0	0	0	0	10	0	0	0	7	2	0	3	0	1702.22
35	4	8	0	0	6	3	0	3	0	0	0	13	3	0	0	10	2	0	3	3	1520.14
39	6	12	0	0	10	4	0	4	0	0	0	18	4	0	0	13	2	0	5	4	2040.51
40	6	12	0	0	10	5	0	5	0	0	0	19	5	0	0	14	2	0	5	5	2049.70
42	4	4	4	0	4	0	0	0	0	0	0	4	0	0	0	3	0	1	2	0	951.79
43	4	8	0	0	8	0	0	0	0	0	0	8	0	0	0	5	0	1	4	0	1755.18
46	4	8	0	0	8	4	0	4	0	0	0	12	4	0	0	9	0	1	4	4	1491.13
48	6	6	6	0	6	3	0	3	0	0	0	9	3	0	0	7	0	1	3	3	960.40
50	6	12	0	0	12	6	0	6	0	0	0	18	6	0	0	13	0	1	6	6	1856.09

DB：double bond，TB：triple bond，Ust.：unsaturability，No.：numbers，R：ring.

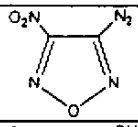
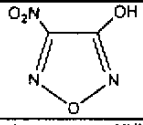
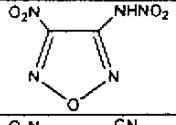
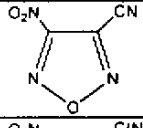
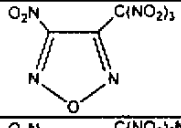
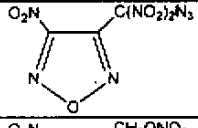
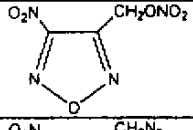
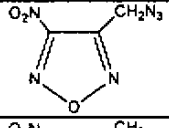
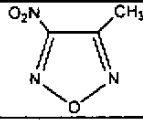
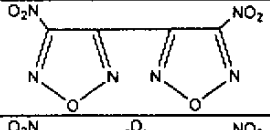
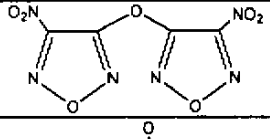
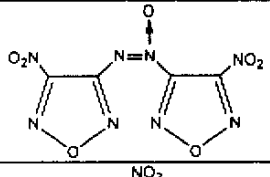
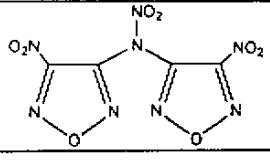
$$Y = 116.8831 - 20.91791X_1 + 39.33009X_2 + 8.467659X_3 + 72.14294X_4 - 82.12151X_5$$
$$- 7.144741X_6 - 108.3784X_7 + 63.72467X_8 + 88.17025X_9 + 66.83949X_{10}$$
$$- 46.36411X_{11} - 15.92694X_{12} - 44.25409X_{13} + 17.25885X_{14} + 101.934X_{15}$$
$$- 75.83083X_{16} + 163.0561X_{17} + 0.4212016X_{18} + 310.0187X_{19} + 54.0352X_{20}$$
$$N = 31, \quad R = 0.9954$$

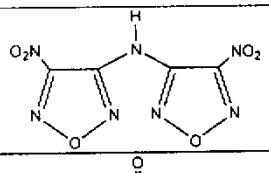
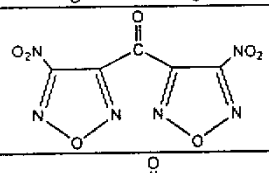
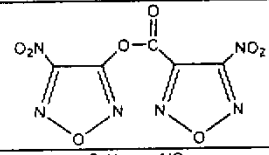
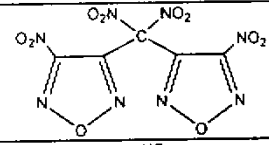
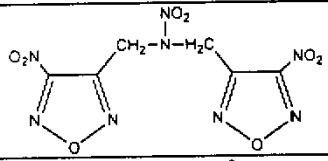
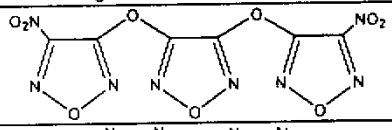
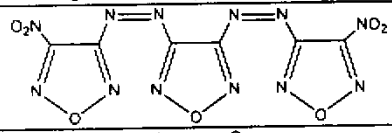
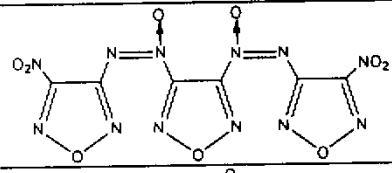
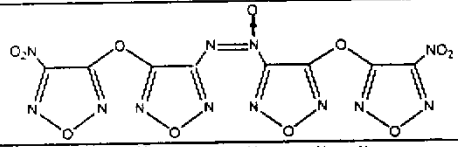
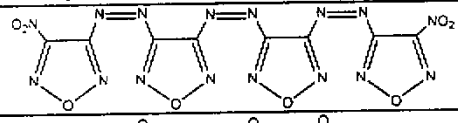
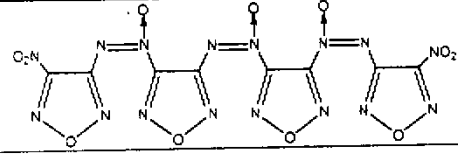
3.2 计算结果

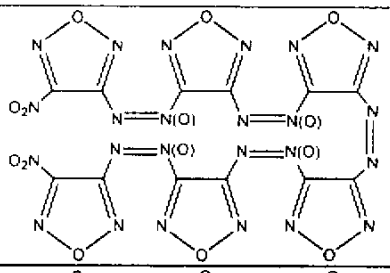
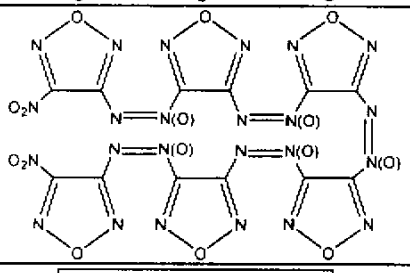
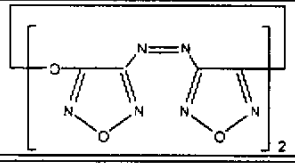
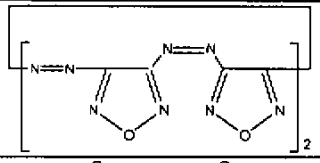
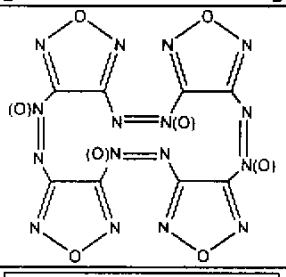
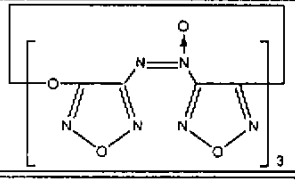
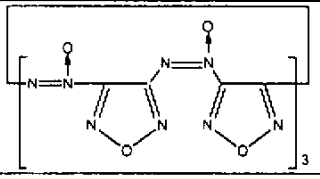
我们根据的硝基呋咱化合物分子结构用分子子图法计算出它们的生成热，与文献的生成热数据相比较，结果 85% 的相对误差在 10% 以内(见表 2).

表 2　硝基呋咱化合物生成热的文献值与计算值的比较(kJ/mol)

Table 2　Comparison of reference and calculated values of the formation heats of nitro furazan compounds(kJ/mol)

No.	Compounds	References	Calculated	Error	Error %
2		530.48	530.889	-0.409	-0.07643
3		261.92	261.873	0.047	0.017555
4		494.83	494.824	0.006	0.000845
5		208.33	208.323	0.007	0.004013
6		292.60	323.239	-30.639	-10.4714
7		608.86	563.297	45.563	7.48318
8		43.26	43.677	-0.417	-0.95652
9		395.05	441.425	-46.375	-11.7384
10		171.05	140.431	30.619	17.89834
12		352.00	351.985	0.015	0.003563
13		294.36	422.778	-128.418	-43.6282
15		620.35	733.837	-113.487	-18.2932
16		367.38	367.426	-0.046	-0.01252

No.	Compounds	References	Calculated	Error	Error %
17		487.05	486.983	0.067	0.01459
20		445.25	445.245	0.005	0.001878
21		327.04	327.047	−0.007	−0.00128
22		328.42	328.385	0.035	0.011455
24		397.73	398.550	−0.820	−0.20704
25		415.99	406.133	9.857	2.370378
26		1227.83	1240.570	−12.740	−1.03731
27		1098.84	1028.251	70.598	6.423844
31		813.80	700.547	113.253	13.917
34		1702.22	1641.143	61.077	3.588144
35		1502.14	1442.129	78.011	5.13185

No.	Compounds	References	Calculated	Error	Error %
39		2040.51	2137.117	-96.607	-4.73451
40		2049.70	2030.958	18.743	0.914634
42		951.79	941.2156	10.5744	1.110584
43		1755.18	1775.6523	-20.4723	-1.16628
46		1491.13	1351.0145	140.1155	9.396687
48		960.40	1006.6661	-46.2661	-4.81772
50		1856.09	1939.8427	-83.7527	-4.51248

3.3　方法的比较

我们以硝基呋咱基团为母体进行分子子图编码法，估算硝基呋咱化合物的生成热达到了较高的精度，相关系数为 0.9954. 在探索的过程中，我们曾以硝基呋咱为母体进行分子子图编码法计算，预估的精度较差，回归方程的相关系数为 0.9873. 由此看来，选择适当的基团为母体进行分子子图编码，是提高预估精度的重要手段之一.

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Estimation and Prediction on Heats of Formation for Nitro Furazan Series Compounds with Novel Molecular Subgraph

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Abstract The molecular structure of nitro furazan compounds was described by a novel coding method on the basis of molecular sub-graph. In this coding method, furazan is considered to be the main-graph, and nitro-, azido-, metho-, and cyano- are dismembered into atoms such as carbon, hydrogen, oxygen and nitrogen (the so called dismembered atoms), which are the sub-graph. For a furazan compound, the formation heat is dependent on the dismembered atoms, carbon-carbon double or triple bond, the numbers of nitryl, ring (unless furazan ring), nitrogen-nitrogen or nitrogen-oxygen double bound, and so on. It has been shown that there exists very good correlation between the coding and the formation heats of nitro furazan compounds. The correlation coefficient (R) of MLR equation for quantitative structure-property relation(QSPR) on the formation heats nitro furazan compounds is 0.9954.

Key words Molecular subgraph, QSPR, Nitro furazan compounds, Heats of formation

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