第 14 卷 第 4 期
2006 年 8 月

含 能 材 料
CHINESE JOURNAL OF ENERGETIC MATERIALS

Vol. 14, No. 4
August, 2006

文章编号：1006-9941(2006)04-0290-04

分子拓扑法预估多硝基烷烃化合物的生成焓

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摘要：以硝基烷烃分子结构中不同基团作为描述码，以每一个描述码作为相应的分子子图项，进行了多元线性回归，预估多硝基烷烃化合物的生成焓，取得了较好的结果，其回归方程相关系数达到 0.9980，绝大多数计算结果的相对误差在 10% 以内。

关键词：物理化学；分子子图；生成焓；烷烃多硝基化合物；多元线性回归；分子结构描述码(MSD)

中图分类号：O642.3　　**文献标识码**：A

1 引 言

热力学数据是化学计算与工程设计中常用到的基础数据[1,2]。生成焓是重要的基础数据之一，由多硝基化合物的生成焓，可计算出推进剂的比冲、特征速度等能量特性参数[3]，还可计算出炸药的爆压、爆速等爆轰参数。而这些数据分散在各种手册或文献中不易查找，合成和实验研究又需要花费大量经费，为此发展了许多预估方法[4,5]，如分子子图法、基团贡献法等[6,7]。这些定量结构性质关系(QSPR)的研究具有重要的理论意义和实际应用价值。近几年来，利用分子拓扑信息来预测分子的某些物化性质是 QSPR 研究的一个重要方面[8]。李良超[9]等通过确立链烷的 5 个分子参数，以其为独立参量，使用回归方法建立模型，预测了链烷的原子化焓、气态标准生成焓、汽化焓和摩尔体积等物理化学性质。冯长君[10]等提出染色的原子序数连接性拓扑指数，对其与烷基衍生物的标准生成焓的相关性进行了研究。本文用分子拓扑法来研究高能量化合物的生成焓计算。

2 分子拓扑指数原理与方法

拓扑指数直接建立在分子子图的基础上，将各子图所含信息转换为新拓扑指数的元素，而不是进行复杂的数学处理，因而在保持分子拓扑信息、提高选择性系数、减少计算工作量等方面具有特色。生成拓扑指数的基本思路是：依照分子拓扑学的原理和方法，将分子图形分解为多个子图，直接将子图进行分类、计数、编码。再将保持部分结构信息的已数字化的子图编码〔新拓扑指数〕与化合物的具体性质相关联，即将化合物结构的新拓扑指数与其性能($\Delta_f H^\Theta$)直接关联。对拓扑分子子图进行分解时应遵循“取大优先，能连不散”的原则，编出的描述码具有如下性质：(1) 不变性：即每种分子的拓扑图分解后只有一种子图表示方式。(2) 唯一性：不同分子的子图编码表达不重复。(3) 简易性：拓扑图的分解方法应简单易行。分子结构信息数值化是最重要的参数，它能反映分子的结构特征，具有通用性，简便，灵活，不依赖于实验。为此我们列出了多硝基烷烃化合物分子结构描述码(见表 1 和表 2)。

2.1 多元线性回归法

我们用多元线性回归程序，以硝基烷烃的拓扑指数(分子子图)码为自变量(共 12 个)，其生成焓的实验值(即文献值)为因变量，进行预估，结果如下：$Y = 119.367 - 253.347a_1 + 25.159a_2 - 25.849a_3 - 124.184a_4 + 149.810a_5 - 151.796a_6 + 14.762a_7 - 278.762a_8 + 34.829a_9 - 39.717a_{10} - 75.130a_{11} - 91.392a_{12}$，(相关系数 $R = 0.9980$，统计检验 $F = 689.933$)，其中 $a_1 \sim a_{12}$ 分别对应 12 个分子子图项，Y 为预测值，其计算结果如表 3 和图 1 所示。

表 1 多硝基烷烃分子结构描述码

Table 1 Molecular structure descriptor of polynitro compounds

a_1	a_2	a_3	a_4	a_5	a_6
—F	—C(H)—	—CH_2—	—CH_3	—C(—)—	—O—
a_7	a_8	a_9	a_{10}	a_{11}	a_{12}
—N(NO_2)—	—OH	—C(NO_2)—	O_2N—C(NO_2)—	O_2N—C(NO_2)—C(NO_2)—	H—

收稿日期：2006-01-09；**修回日期**：2006-04-03

基金项目：国防科技重点实验室基金项目(5155060101QT5102)

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表 2　各种多硝基烷烃化合物的 MSD 编码

Table 2　MSD code of various polynitro compounds

comp. No.	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}	a_{11}	a_{12}
1	1	0	0	0	0	0	0	0	0	0	1	0
2	1	0	0	0	0	0	0	0	0	1	0	1
3	0	0	0	0	0	0	0	0	0	1	0	2
4	0	0	0	0	0	0	0	0	1	0	0	3
5	0	0	0	1	0	0	0	0	0	1	0	1
6	0	0	0	0	0	0	0	0	2	0	0	4
7	0	0	0	1	0	0	0	0	1	0	0	2
8	0	0	1	1	0	0	0	0	0	1	0	1
9	0	0	1	0	0	0	0	0	2	0	0	4
…	…	…	…	…	…	…	…	…	…	…	…	…
39	0	0	1	0	0	0	0	1	0	0	1	0
40	0	0	5	0	0	1	1	0	0	0	2	0
41	0	0	4	0	0	3	0	0	0	0	2	0

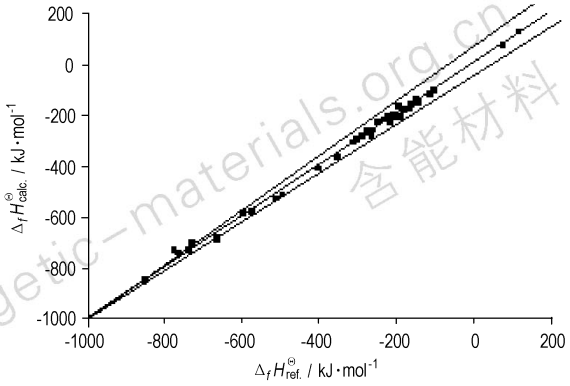
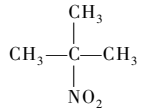
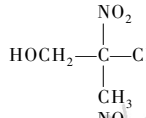
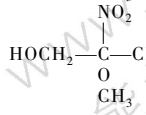


图 1　硝基烷烃的生成焓实验与预测结果比较图

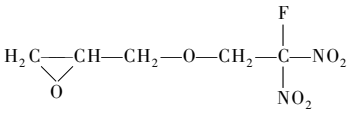
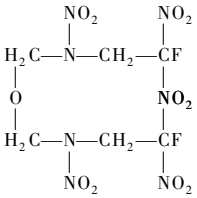
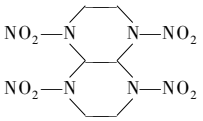
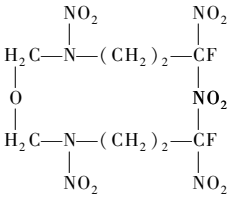
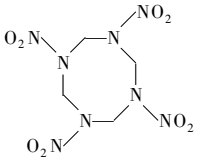
Fig. 1　Comparison of the reference and calculation values of enthalpy of formation for polynitro compounds

表 3　硝基烷烃的生成焓

Table 3　The enthalpy of formation for polynitro compounds

No.	structure	compound name	formula	state	$\Delta_f H^{\Theta}$/kJ·mol^{-1} ref.[3]	$\Delta_f H^{\Theta}$/kJ·mol^{-1} calc.	error%
1	$FC(NO_2)_3$	fluorotrinitromethane	CFN_3O_6	l	−220.7	−209.11	−5.25
2	$FCH(NO_2)_2$	fluorodinitromethane	$CHFN_2O_4$	l	−277.8	−265.09	−4.58
3	$CH_2(NO_2)_2$	dinitromethane	$CH_2N_2O_4$	l	−104.9	−103.13	−1.68
4	CH_3NO_2	nitromethane	CH_3NO_2	l	−112.6	−119.98	6.55
5	$(NO_2)_2CHCH_3$	1,1-dinitroethane	$C_2H_4N_2O_4$	l	−148.2	−135.93	−8.28
6	$NO_2CH_2CH_2NO_2$	1,2-dinitroethane	$C_2H_4N_2O_4$	s	−177.7	−176.54	−0.65
7	$CH_3CH_2NO_2$	nitroethane	$C_2H_5NO_2$	l	−143.9	−152.77	6.17
8	$(NO_2)_2CHCH_2CH_3$	1,1-dinitropropane	$C_3H_6N_2O_4$	l	−163.2	−161.78	−0.87
9	$NO_2CH_2CH_2CH_2NO_2$	1,3-dinitropropane	$C_3H_6N_2O_4$	l	−207.1	−202.39	−2.27
10	$CH_3C(NO_2)_2CH_3$	2,2-dinitropropane	$C_3H_6N_2O_4$	s	−192.5	−168.72	−12.35
11	$CH_3CHNO_2CH_3$	2-nitropropane	$C_3H_7NO_2$	l	−180.3	−185.56	2.92
12	$(NO_2)CH_2CH_2CH_3$	1-nitropropane	$C_3H_7NO_2$	l	−167.2	−178.62	6.83
13	$(NO_2)_2FCCH_2N(NO_2)CH_2C(NO_2)_3$	1-fluro-1,1,3,5,5,5-hexanitro-3-azapentane	$C_4H_4FN_7O_{12}$	s	−263.5	−285.76	8.45
14	$CH_3CHNO_2(CH_2)_7CH_3$	2-nitrodecane	$C_{10}H_{21}NO_2$	l	−351.5	−366.51	4.27
15	$CH_3C(NO_2)_2C(NO_2)_2CH_3$	2,2,3,3-tetranitrobutane	$C_4H_6N_4O_8$	s	−189.7	−208.44	9.88
16	$NO_2CH_2CH_2CH_2CH_3$	1-nitrobutane	$C_4H_9NO_2$	l	−192.5	−204.47	6.22
17	$CH_3CH(NO_2)CH_2CH_3$	2-nitrobutane	$C_4H_9NO_2$	l	−207.5	−211.41	1.89
18		2-methyl-2-nitropropane	$C_4H_9NO_2$	s	−229.8	−218.36	−4.98
19		2-nitro-2-methyl-1,3-propanediol	$C_4H_9NO_4$	s	−574.4	−579.21	0.84
20		2-hydroxymethyl-2-nitro-1,3-propanediol	$C_4H_9NO_5$	s	−735.5	−731.01	−0.61
21	$(NO_2)_2FCCH_2OCH_2OCH_2CF(NO_2)_2$	1,1-dinitro-2-(2-fluorin-2,2-dinitroethoxy)methoxy-1-fluoroethane	$C_5H_6F_2N_4O_{10}$	l	−849	−847.90	−0.13
22	$(NO_2)_2FCCH_2N(NO_2)CH_2OCH_2CF(NO_2)_2$	1,7-difluoro-1,1,3,7,7-pentanitro-3-aza-5-oxaheptane	$C_5H_6F_2N_6O_{11}$	s	−663.3	−681.34	2.72
23	$(NO_2)_2FCCH_2N(NO_2)CH_2N(NO_2)CH_2CF(NO_2)_2$	1,7-difluoro-1,1,3,5,7,7-hexanitro-3,5-diazaheptane	$C_5H_6F_2N_8O_{12}$	s	−494.7	−514.78	4.06
24	$(NO_2)_3CCH_2OCH_2OCH_2C(NO_2)_3$	bis(2,2,2-trinitroethoxy)-methane	$C_5H_6N_6O_{14}$	s	−403.3	−412.03	2.17

续表 3

No.	structure	compound name	formula	state	$\Delta_f H^\Theta$/kJ·mol^{-1} ref.[3]	$\Delta_f H^\Theta$/kJ·mol^{-1} calc.	error%
25		(2-fluoro-2, 2-dinitroethoxy) methyloxirane	$C_5H_7FN_2O_6$	l	-510.8	-529.68	3.70
26	$(NO_2)_2CH(CH_2)_3CH_3$	1,1-dinitropentane	$C_5H_{10}N_2O_4$	l	-216.9	-213.47	-1.58
27	$NO_2CH_2C(CH_3)_2CH_2NO_2$	2,2-dimethyl-1,3-dinitro-propane	$C_5H_{10}N_2O_4$	s	-275.1	-275.10	0.0004
28	$NO_2CH_2(CH_2)_3CH_3$	1-nitropentane	$C_5H_{11}NO_2$	l	-215.4	-230.32	6.93
29	$(NO_2)_2FCCH_2CH_2N(NO_2)CH_2OCH_2CF(NO_2)_2$	1,8-difluoro-1,1,4,8,8-pentanitro-4-aza-6-oxaoctane	$C_6H_8F_2N_6O_{11}$	s	-726.4	-707.19	-2.64
30	$(NO_2)_2FCCH_2OCH_2NNO_2CH_2OCH_2CF(NO_2)_2$	1,9-difluoro-1,1,5,9,9-pentanitro-3,7-dioxa-5-azanonane	$C_6H_8F_2N_6O_{12}$	s	-851.9	-858.99	0.83
31		1,1′-oxybis(2,4,4-trinitro-4-fluoro-2-azabutane)	$C_6H_8F_2N_8O_{13}$	s	-663.6	-692.43	4.34
32		1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin	$C_6H_{10}N_8O_8$	s	115.9	125.34	8.14
33	$(CH_3)_2NO_2CC(NO_2)_2CH_2CH_3$	2-methyl-2,3,3-trinitropentane	$C_6H_{11}N_3O_6$	s	-290.3	-283.92	-2.20
34	$(CH_3)_2NO_2CCNO_2(CH_3)_2$	2,3-dimethyl-2,3-dinitrobutane	$C_6H_{12}N_2O_4$	s	-311.5	-307.71	-1.22
35	$(NO_2)_2FCCH_2CH_2N(NO_2)CH_2OCH_2CH_2CF(NO_2)_2$	1,9-difluoro-1,1,4,9,9-pentanitro-4-aza-6-oxanonane	$C_7H_{10}F_2N_6O_{11}$	s	-775.6	-733.04	-5.49
36		1,1′-oxybis(2,5,5-trinitro-5-fluoro-2-azapentane)	$C_8H_{12}F_2N_8O_{13}$	s	-763.7	-744.13	-2.56
37	$NO_2CH_2(CH_2)_2CH_2NO_2$	1,4-dinitrobutane	$C_4H_8N_2O_4$	s	-249.20	-228.24	-8.41
38		cyclotetramethylenetetranitramine	$C_4H_8N_8O_8$	s	75.02	75.02	-0.001
39	$(O_2N)_3CCH_2OH$	2,2,2-trinitroethanol	$C_2H_3N_3O_7$	s	-261.00	-260.37	-0.24
40	$(O_2N)_3CCH_2CH_2N(NO_2)CH_2OCH_2C(O_2N)_3$	(*N*-nitro-3,3,3-trinitropropyl aminomethyl-3,3,3-trinitropropyl) ether	$C_7H_{10}N_8O_{15}$	s	-303.70	-297.17	-2.15
41	$(O_2N)_3CCH_2OCH_2OCH_2OCH_2C(O_2N)_3$	bis(2,2,2-trinitroethoxy)methylether	$C_6H_{8\cdot6}O_{16}$	s	-596.90	-589.68	-1.21

2.2 相关矩阵与变量独立性

自变量之间的相关性可以分为强正相关、强负相关、弱相关和不相关。相关系数在 0 到 1 之间,代表了从完全不相关到完全相关。回归方程中各变量的协方差矩阵(见表 4)中的多数相关系数都远小于 1,说明了多数分子子图之间没有特定的相关性,有较大的可替换性。但也有个别分子子图对的相关系数明显高于平均值。作为多硝基烷烃的结构描述码,12 种分子子图在不同类型的多硝基烷烃中的相关性反映了这些结构描述码间的匹配规则,代表了多硝基烷烃的结构特征。同一类型的多硝基烷烃中各种分子子图的数量可以有较大的变化,但分子子图的数量变化有一定的相互制约性,遵循一定的相关关系。一种分子子图与某些分子子图连接的频率可能高一些,而与另一些分子子图连接的频率低一些。分子拓扑指数描述码应具有唯一性、独立性,它选择恰当与否直接影响预估精度。为此要求所选的分子结构描述码必须能反映物质的结构特征,描述码的邻、间、对的位置也会有影响,必须仔细研究。

表 4　回归方程中各变量的协方差矩阵

Table 4　Covariance matrix of the variables in MLR

	Y	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}	a_{11}	a_{12}
Y	1.000	-0.746	0.219	-0.504	0.240	0.044	-0.713	0.020	-0.257	0.243	-0.595	-0.047	0.401
A1	-0.746	1.000	-0.041	0.450	-0.447	-0.096	0.446	0.346	-0.164	-0.466	0.817	-0.129	-0.391
A2	0.219	-0.041	1.000	0.183	-0.157	-0.034	0.064	0.471	-0.058	-0.164	-0.086	-0.083	-0.146
A3	-0.504	0.450	0.183	1.000	-0.380	-0.171	0.505	0.519	-0.035	-0.367	0.294	0.195	-0.375
A4	0.240	-0.447	-0.157	-0.380	1.000	0.191	-0.389	-0.361	0.011	0.451	-0.244	-0.286	-0.041
A5	0.044	-0.096	-0.034	-0.171	0.191	1.000	-0.091	-0.078	-0.043	0.330	-0.128	-0.062	0.382
A6	-0.713	0.446	0.064	0.505	-0.389	-0.091	1.000	0.039	-0.014	-0.392	0.318	0.454	-0.389
A7	0.020	0.346	0.471	0.519	-0.361	-0.078	0.039	1.000	-0.133	-0.376	0.237	-0.061	-0.335
A8	-0.257	-0.164	-0.058	-0.035	0.011	-0.043	-0.014	-0.133	1.000	0.101	-0.218	-0.009	-0.183
A9	0.243	-0.466	-0.164	-0.367	0.451	0.330	-0.392	-0.376	0.101	1.000	-0.575	-0.298	0.718
A10	-0.595	0.817	-0.086	0.294	-0.244	-0.128	0.318	0.237	-0.218	-0.575	1.000	-0.262	-0.410
A11	-0.047	-0.129	-0.083	0.195	-0.286	-0.062	0.454	-0.061	-0.009	-0.298	-0.262	1.000	-0.265
A12	0.401	-0.391	-0.146	-0.375	-0.041	0.382	-0.389	-0.335	-0.183	0.718	-0.410	-0.265	1.000

3　结　论

综上所述，以多硝基化合物中的分子结构作为拓扑指数的描述码，进行多元线性回归，建立起多元线性回归方程，以此方程可以迅速方便地计算出多硝基烷烃化合物的生成焓，并可预估许多新的多硝基烷烃化合物的生成焓，为设计新的含能材料打下基础，具有实用意义和推广价值。

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Development and Application of Single-wavelength Pyrometer Used for Evaluating the Effects of Thermal Damage

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Abstract: A single-wavelength pyrometer used for evaluating the effects of thermal damage was developed, which offered a new method to describe the temperature changes of explosive products during the course of the explosion. The temperature of oxyacetylene flame was simultaneously measured by the pyrometer and a thermocouple. And the measurement error of the single-wavelength pyrometer is only 6.2%. The results indicate that the emissivity has little effect on temperature measurement of the oxyacetylene flame by the pyrometer. The pyrometer was aslo used to measure explosive products temperature of TNT. The curve of thermal damage of TNT was obtained, which shows the temperature changes of the explosive products of TNT, and the peak temperature of the curve is 3167.15 K.

Key words: explosion mechanics; single-wavelength pyrometer; explosive product; thermal damage

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Prediction of Enthalpy of Formation for Polynitro Compounds by Using Molecular Subgraph

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Abstract: The enthalpies of formation for polynitro compounds were predicted by using the molecular structure describers (MSD). With the different groups of polynitro compound molecules acting as descriptor codes (i.e. molecular subgraphs), multiple linear regression equation was established, of which the correlation coefficient is 0.9980. Most of the relative errors of the calculated values are within 10%. It can be seen that the calculated values of the enthalpies of formation are in good agreement with the experimental values.

Key words: physical chemistry; molecular subgraph; enthalpy of formation; polynitro compound; multiple linear regression; molecular structure describer (MSD)

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Matching Relation Between Artificial Viscosity and Mesh Size in Numerical Modeling of Detonation of Insensitive High Explosives

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Abstract: In numerical modeling of the plane detonation wave, the state behind steady detonation must be in agreement with the Chapman-Jouguet theory. The modified JWL equation of states (EOS) of the products and Hybrid reaction model are used to obtain the matching relation between artificial viscosity and mesh size of PBX9502 of insensitive high explosives and are compared with other reaction models. When this condition is satisfied, the detonation velocity and the state of sound speed point including pressure, density and internal energy can be in agreement with the C-J theory. These variables are independent of mesh size. Thus the mesh size can be larger, and the matching relation can be used in practice.

Key words: explosion mechanics; insensitive high explosive; artificial viscosity; mesh size