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外电场中1,4-二硝基咪唑-*N*-氧化物感度的理论研究

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摘 要: 为探明外电场中炸药感度的变化规律,借助B3LYP/6-311++G(2d,p)和M06-2X/6-311++G(2d,p)理论方法,研究了外电场方向和强度的变化对1,4-二硝基咪唑-*N*-氧化物(1,4-DNIO)炸药潜在引发键的键长、硝基电荷、键离解能及撞击感度、静电火花感度和冲击起爆压力的影响。结果表明,在无电场和外电场作用下,N—NO_2是最可能的引发键,其次是N→O,最后是C—NO_2键。沿N→O、C—NO_2键轴正方向和N—NO_2负方向的外电场使N→O和C—NO_2键离解能减小、N—NO_2键离解能增大、H_{50}增大、撞击感度降低;与上述反方向的外电场对引发键强度和撞击感度的影响正好相反。引发键键长、AIM电子密度、硝基电荷、键离解能和H_{50}的变化量分别与外电场强度之间呈良好的线性关系,大多数情况下,相关系数$R^2>0.9500$。外电场对电火花感度和冲击起爆压力的影响不大,外电场由-0.010 a.u.变化到0.010 a.u.,变化值分别小于0.5 J和0.15 MPa。

关键词: 1,4-二硝基咪唑-*N*-氧化物(1,4-DNIO);感度;外电场;密度泛函;表面静电势

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1 引 言

外电场可提高炸药爆轰波阵面附近气体能量、增大炸药爆速和爆压[1-2],而且其在炸药体系中的应用已受到了人们的青睐[3]。然而,炸药在制备、加工、运输、储存和使用过程中可能发生电场事故的安全问题,导致目前向炸药体系引入外电场的许多关键技术仍难以突破[4-5]。为了探明外电场中炸药感度的变化规律,将外电场安全有效地引入炸药体系,近年来人们对外电场中炸药感度的研究工作展开了从实验到理论、宏观到微观、热力学到动力学全方位的探索[5-8]。例如,俄罗斯科学家Rodzevich等[5]借助实验方法研究了外电场对叠氮化银分解速率的影响。Politzer[9-11]和宋晓书[12]等采用密度泛函理论(DFT)方法研究了几种单质炸药分子在电场中的偶极矩、引发键伸缩振动频率和静电势等的变化趋势。杨明理等[13-14]借助DFT方法讨论了外电场对CH_3NO_2和1,1-二氨基-2,2-二硝基乙烯(FOX-7)引发键C—NO_2断裂反应的影响。近年来,任福德等借助DFT-B3LYP和MP2方法比较了外电场对CH_3NO_2和NH_2NO_2[15]、2,4,6-三硝基甲苯(TNT)和黑索今(RDX)[16]分子中的C/N—NO_2、C/N—H键和硝基中N—O键强度的影响,探讨了外电场中奥克托今(HMX)/FOX-7共晶体系结合能的变化[17]及CH_3NO_2的分解反应动力学[7-8]。

对于存在多个化学键强度相差不大的潜在引发键的炸药分子,外电场方向和强度的改变可能导致引发键类型的改变[6-8,15]。探明外电场对该类炸药分子潜在引发键强度和类型的影响,对于正确预测其在外电场中的感度是必要的。

N→O配位键是炸药潜在的引发键之一[18]。理论研究表明[19],硝基咪唑环3-位氮原子形成N→O配位键的*N*-氧化物爆轰性能可优于六硝基六氮杂异伍兹烷(CL-20)。为此,本研究选择1,4-二硝基咪唑-*N*-氧化物(1,4-DNIO)为目标物质,探讨外电场方向和强度对N→O、N—NO_2、C—NO_2和C—H键强度影响,确定外电场中的引发键,预测撞击感度、静电火花感度

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和冲击起爆压力随外电场方向和强度改变的变化规律,以期为将外电场引入含有N→O配位键分子的含能材料体系而避免偶然爆炸的技术提供理论指导。

2 计算方法

所有计算均采用Gaussian 09程序包[20]完成。借助B3LYP/6-311++G(2d,p)和M06-2X/6-311++G(2d,p)理论方法进行了分子的结构优化和AIM(atoms in molecules)[21]、Mulliken电荷、APT(atomic polar tensors)电荷、前线轨道、分子表面静电势[22]分析以及撞击感度、静电火花感度和冲击起爆压力的预测。

由于垂直于引发键方向的外电场对引发键强度的影响不显著[15],本研究仅选择了平行于N→O、N—NO_2和C—NO_2潜在引发键方向的外电场,电场强度分别为±0.002,±0.004,±0.006,±0.008,±0.010 a.u.(表1)。电场的正方向规定从给电子体指向吸电子体的方向为正方向。因此,对于N→O、N—NO_2和C—NO_2的电场方向,正方向分别是指由N原子指向O、N和C指向硝基N原子(图1)。

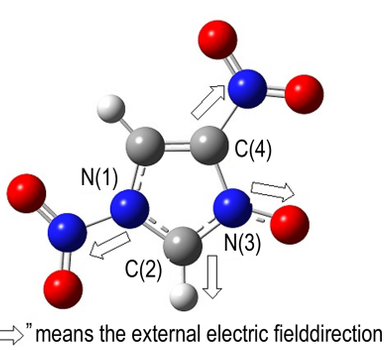

图1 1,4-DNIO的结构及外电场方向

Fig. 1 Structure and external electric field directions for 1,4-DNIO

3 结果与讨论

3.1 结构和硝基电荷

炸药感度与引发键的强度、硝基电荷密切相关[23]。为探明外电场中炸药感度的变化规律,首先探讨了外电场方向和强度对1,4-DNIO潜在引发键强度和硝基电荷的影响。

表1给出了1,4-DNIO在电场中的键长、AIM电子密度、Mulliken和APT硝基电荷的理论计算值。可以看出,在两种理论水平上计算得到的键长和AIM电子密度值均接近。在外电场作用下,N(3)→O和N(1)—N键长变化较大,C(4)—N次之,C(2)—H键长几乎没变;与外电场方向平行的化学键键长受电场的影响较显著:沿N(3)→O和C(4)—N(即C—NO_2)键轴正方向的外电场拉长了N(3)→O和C(4)—N键长,缩短了N(1)—N(即N—NO_2)键长;沿N(1)—N键轴正方向的外电场缩短了N(3)→O和C(4)—N键长,拉长了N(1)—N键长;沿N(3)→O、C(4)—N和N(1)—N负方向外电场的键长变化分别与其正方向外电场结果相反;键长改变量(与无电场的键长值之差,ΔR)与外电场强度(E)之间存在良好的线性关系(图2),这与本课题组之前对CH_3NO_2和NH_2NO_2在外电场中的计算结果一致[15]。

在两种理论计算水平上,在外电场作用下,AIM电子密度变化的强度与趋势几乎与之相应的化学键键长变化一致,且其改变量(与无电场的电子密度之差,$\Delta\rho$)与外电场强度(E)之间也存在良好的线性关系(图2)。根据AIM理论[21],化学键临界点的电子密度越大,化学键强度越强,键长越短;反之,电子密度越小,化学键强度越弱,键长越长;而且,电子密度改变越大,键长的变化越显著。此即为外电场中键长变化的本质原因。比较发现,1,4-DNIO中引发键键长和电子密度的变化量及其与外电场强度之间呈线性关系的相关系数R^2值均大于CH_3NO_2和NH_2NO_2在外电场中相应的计算结果[15]。这可能是由于具有$\prod_{12}^{18}$结构的1,4-DNIO中的π电子在外电场中较CH_3NO_2和NH_2NO_2中σ电子更易移动造成的。

大多数情况下,在两种理论计算水平上,沿N(3)→O和C(4)—N键轴正方向的外电场使N—NO_2的硝基Mulliken电荷值(绝对值)增大、APT电荷值减小,而使C—NO_2的硝基Mulliken电荷值减小、APT电荷值增大;沿N(1)—N键轴正方向的外电场使N—NO_2的硝基Mulliken电荷值减小、APT电荷值增大,而使C—NO_2的硝基Mulliken电荷值增大、APT电荷值减小;负方向外电场中,硝基的Mulliken和APT值的变化分别与其正方向外电场结果相反;N—NO_2的硝基电荷变化趋势总与C—NO_2相反,导致外电场中1,4-DNIO分子的偶极矩变大。硝基电荷的改变量(ΔQ)与外电场强度(E)之间呈良好的线性关系(图2)。

表 1 在B3LYP/6-311++G(2d,p)(平滑)和M06-2X/6-311++G(2d,p)(黑体)水平上计算得到的1,4-DNIO在不同电场大小和方向的部分键长,AIM电子密度,Mulliken和APT 硝基电荷

Table 1 Selected bond lengths(R), AIM electron densities(ρ), Mulliken and APT nitro charges (Q) of 1,4-DNIO with different external electric field strengths and orientations at the B3LYP/6-311++G(2d,p) (in flat) and M06-2X/6-311++G(2d,p) (in bold) levels

field	$R_{N(3)\rightarrow O}$/Å	$R_{N(1)-N}$/Å	$R_{C(4)-N}$/Å	$\rho_{N(3)-O}$/a.u.	$\rho_{N(1)-N}$/a.u.	$\rho_{C(4)-N}$/a.u.	Q_{NO2}[a]/e	Q_{NO2}[b]/a.u.
no field	1.2593	1.4282	1.4395	0.4969	0.3508	0.2725	−0.2297(0.4337)	−0.2437(0.0664)
	1.2565	**1.4109**	**1.4403**	**0.5028**	**0.3525**	**0.2678**	**−0.2121(0.4263)**	**−0.2341(0.0332)**
$+0.010_{(N(3)\rightarrow O)}$	1.2955	1.4125	1.4448	0.4839	0.3606	0.2631	−0.2349(0.4302)	−0.2415(0.0685)
	1.2878	**1.3957**	**1.4451**	**0.4883**	**0.3641**	**0.2561**	**−0.2172(0.4248)**	**−0.2317(0.0352)**
$+0.008_{(N(3)\rightarrow O)}$	1.2849	1.4161	1.4428	0.4861	0.3582	0.2635	−0.2343(0.4307)	−0.2418(0.0681)
	1.2786	**1.3981**	**1.4436**	**0.4915**	**0.3603**	**0.2583**	**−0.2158(0.4242)**	**−0.2326(0.0341)**
$+0.004_{(N(3)\rightarrow O)}$	1.2682	1.4222	1.4413	0.4910	0.3535	0.2682	−0.2313(0.4325)	−0.2432(0.0668)
	1.2640	**1.4038**	**1.4419**	**0.4972**	**0.3561**	**0.2638**	**−0.2137(0.4262)**	**−0.2338(0.0333)**
$-0.004_{(N(3)\rightarrow O)}$	1.2537	1.4345	1.4384	0.5005	0.3467	0.2723	−0.2282(0.4342)	−0.2443(0.0660)
	1.2520	**1.4158**	**1.4391**	**0.5067**	**0.3485**	**0.2683**	**−0.2115(0.4270)**	**−0.2345(0.0327)**
$-0.008_{(N(3)\rightarrow O)}$	1.2489	1.4357	1.4360	0.5062	0.3429	0.2763	−0.2262(0.4362)	−0.2460(0.0652)
	1.2471	**1.4183**	**1.4369**	**0.5117**	**0.3441**	**0.2722**	**−0.2101(0.4275)**	**−0.2363(0.0316)**
$-0.010_{(N(3)\rightarrow O)}$	1.2453	1.4393	1.4351	0.5088	0.3384	0.2790	−0.2231(0.4379)	−0.2482(0.0649)
	1.2437	**1.4206**	**1.4358**	**0.5141**	**0.3405**	**0.2749**	**−0.2090(0.4283)**	**−0.2375(0.0310)**
$+0.010_{(N(1)-N)}$	1.2518	1.4708	1.4350	0.5065	0.3375	0.2841	−0.2270(0.4382)	−0.2468(0.0638)
	1.2497	**1.4617**	**1.4365**	**0.5115**	**0.3381**	**0.2773**	**−0.2085(0.4310)**	**−0.2379(0.0305)**
$+0.008_{(N(1)-N)}$	1.2540	1.4519	1.4368	0.5038	0.3410	0.2790	−0.2277(0.4367)	−0.2462(0.0644)
	1.2515	**1.4315**	**1.4377**	**0.5092**	**0.3428**	**0.2731**	**−0.2092(0.4299)**	**−0.2368(0.0316)**
$+0.004_{(N(1)-N)}$	1.2568	1.4353	1.4385	0.5005	0.3472	0.2752	−0.2291(0.4346)	−0.2444(0.0660)
	1.2542	**1.4175**	**1.4392**	**0.5059**	**0.3491**	**0.2704**	**−0.2115(0.4275)**	**−0.2351(0.0327)**
$-0.004_{(N(1)-N)}$	1.2619	1.4176	1.4399	0.4938	0.3536	0.2715	−0.2305(0.4330)	−0.2430(0.0669)
	1.2590	**1.4008**	**1.4417**	**0.5001**	**0.3551**	**0.2663**	**−0.2128(0.4266)**	**−0.2332(0.0338)**
$-0.008_{(N(1)-N)}$	1.2643	1.4068	1.4418	0.4892	0.3561	0.2663	−0.2335(0.4317)	−0.2411(0.0682)
	1.2618	**1.3892**	**1.4435**	**0.4953**	**0.3579**	**0.2622**	**−0.2157(0.4252)**	**−0.2315(0.0354)**
$-0.010_{(N(1)-N)}$	1.2657	1.4021	1.4442	0.4865	0.3583	0.2641	−0.2346(0.4308)	−0.2398(0.0699)
	1.2635	**1.3837**	**1.4457**	**0.4929**	**0.3597**	**0.2618**	**−0.2160(0.4244)**	**−0.2300(0.0356)**
$+0.010_{(C(4)-N)}$	1.2752	1.4221	1.4446	0.4879	0.3613	0.2603	−0.2335(0.4297)	−0.2401(0.0705)
	1.2703	**1.4041**	**1.4452**	**0.4919**	**0.3616**	**0.2547**	**−0.2147(0.4222)**	**−0.2302(0.0368)**
$+0.008_{(C(4)-N)}$	1.2712	1.4233	1.4433	0.4901	0.3579	0.2628	−0.2319(0.4308)	−0.2412(0.0694)
	1.2676	**1.4052**	**1.4443**	**0.4942**	**0.3592**	**0.2572**	**−0.2133(0.4238)**	**−0.2313(0.0359)**
$+0.004_{(C(4)-N)}$	1.2656	1.4253	1.4416	0.4939	0.3537	0.2689	−0.2297(0.4323)	−0.2430(0.0672)
	1.2628	**1.4073**	**1.4417**	**0.4983**	**0.3551**	**0.2637**	**−0.2116(0.4263)**	**−0.2335(0.0339)**
$-0.004_{(C(4)-N)}$	1.2548	1.4329	1.4381	0.5033	0.3456	0.2752	−0.2293(0.4344)	−0.2446(0.0652)
	1.2519	**1.4145**	**1.4387**	**0.5048**	**0.3505**	**0.2699**	**−0.2112(0.4268)**	**−0.2351(0.0328)**
$-0.008_{(C(4)-N)}$	1.2493	1.4375	1.4359	0.5083	0.3410	0.2797	−0.2280(0.4356)	−0.2485(0.0634)
	1.2475	**1.4191**	**1.4361**	**0.5091**	**0.3449**	**0.2747**	**−0.2096(0.4281)**	**−0.2366(0.0317)**
$-0.010_{(C(4)-N)}$	1.2458	1.4386	1.4338	0.5116	0.3391	0.2830	−0.2271(0.4365)	−0.2488(0.0629)
	1.2446	**1.4235**	**1.4340**	**0.5127**	**0.3418**	**0.2789**	**−0.2092(0.4286)**	**−0.2379(0.0311)**

Note: a) Mulliken and APT(in parentheses) charges of the —NO_2 group involving the N—NO_2 moiety. b) Mulliken and APT charges of the —NO_2 group involving the C—NO_2 moiety.

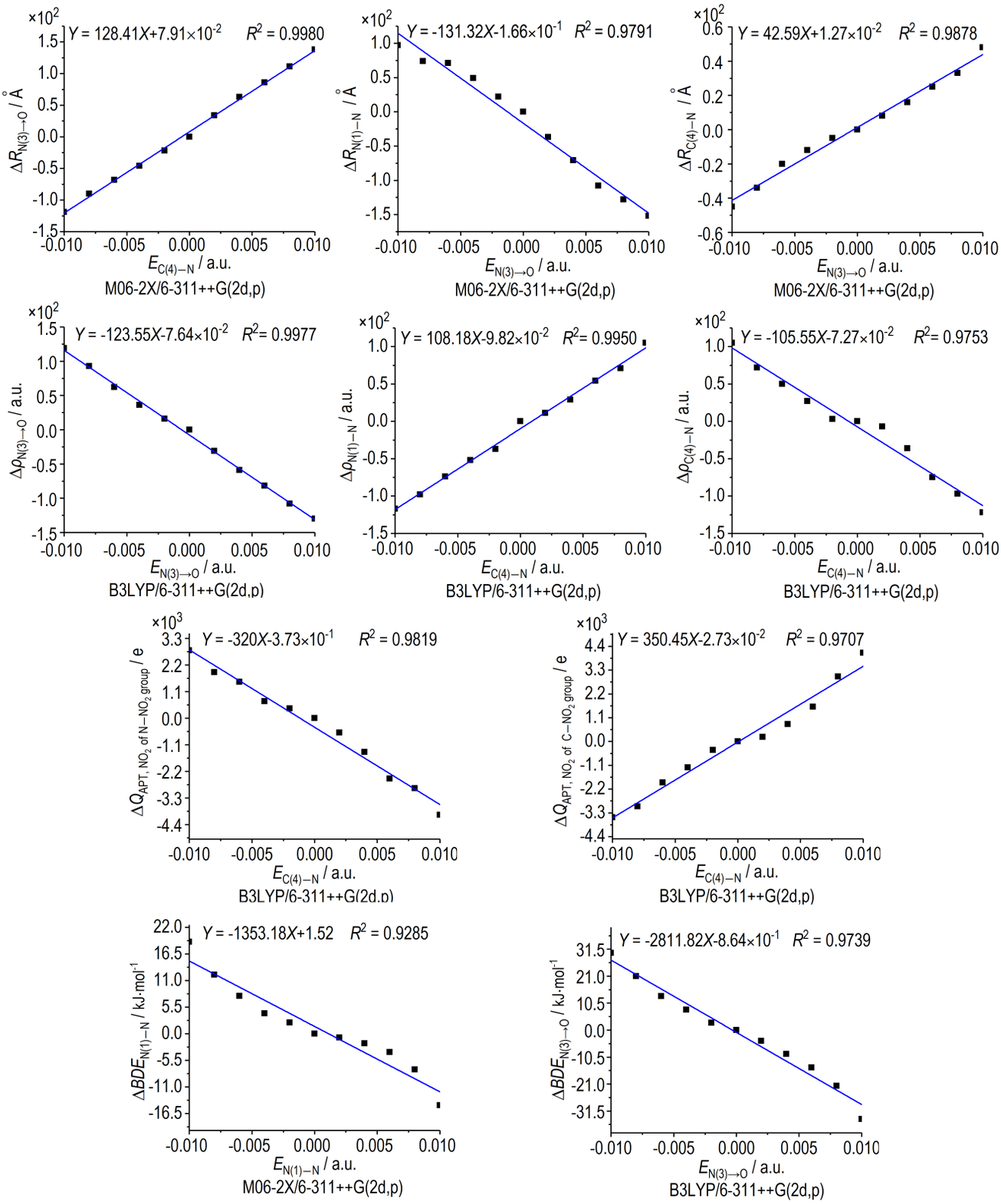

图 2 键长变化量(Δ*R*)、AIM电子密度变化量(Δ*ρ*)、硝基电荷变化值(Δ*Q*)、键离解能变化值(ΔBDE)与外电场强度(*E*)之间的线性关系

Fig. 2 Changes in the bond lengths (Δ*R*), electron densities (Δ*ρ*), nitro charges (Δ*Q*), bond dissociation energy (Δ*BDE*) versus field strengths (E) in different fields

3.2 引发键离解能

炸药引发键离解能与感度密切相关[24-25]。因此,本研究探讨了1,4-DNIO在外电场中潜在引发键离解能的变化(表2),其中,对于R→O键的离解能,采用三重态氧进行计算。

大多数情况下,在两种理论计算水平上,随着外电场强度的改变,与电场方向平行的引发键离解能变化较明显;沿N(3)→O和C(4)—N键轴正方向的外电场使N(3)→O和C(4)—N键离解能减小、使N(1)—N键离解能增大;沿N(1)—N键轴正方向的外电场增大了N(3)→O和C(4)—N键离解能、减弱了N(1)—N键离解能;负方向外电场中的键离解能的变化分别与其正方向外电场变化相反。在外电场作用下,N(3)→O和N(1)—N键离解能变化较大,C(4)—N次之,C(2)—H键离解能几乎没有变化。这些结果均佐证了外电场中引发键键长和AIM电子密度的计算结果。键离解能的变化量(ΔBDE)与外电场强度(E)之间存在良好的线性关系(图2)。

在两种理论水平上的计算结果均表明,在无电场和外电场作用下,1,4-DNIO中引发键的离解能均遵循以下顺序:$BDE_{N(1)-N}$<<$BDE_{N(3)\rightarrow O}$<$BDE_{C(4)-N}$<<$BDE_{C(2)-H}$。这表明,1,4-DNIO起爆反应中N(1)—NO_2键首先断裂,其次是N(3)→O,C(4)—NO_2和C(2)—H键不易断裂。因此,在无电场和外电场作用下,1,4-DNIO最可能的引发键为N(1)—NO_2键,其次是N(3)→O键,C(4)—NO_2和C(2)—H成为引发键的可能性较小。

在无电场和外电场作用下,1,4-DNIO中N—NO_2引发键离解能小于100.0 kJ·mol^{-1}(除沿N(1)—N负方向且强度为0.010 a.u.的电场外)。一般地,非芳香环上的N—NO_2键离解能接近200.0 kJ·mol^{-1}[26]。为解释1,4-DNIO芳香环上N—NO_2离解能小的原因,进行了其环中心NICS(nucleus-independent chemical shift)(NICS(0,π))[27]计算。一般地,NICS(0,π)值越大,单双键共振程度和芳香性越强,分子或自由基越稳定。在M06-2X/6-311++G(2d,p)水平上,沿N(1)—N键轴方向电场强度从-0.010 a.u.变化到0.010 a.u.(步长为0.002 a.u.),由1,4-DNIO的N—NO_2键均裂生成的4-硝基咪唑-*N*-氧化物自由基的NICS(0,π)值分别为-4.82、-4.76、-4.75、-4.75、-4.74、-4.74、-4.74、-4.74、-4.73、-4.73、-4.72。这些值均接近配位O在1-位氮原子上的4-硝基咪唑-*N*-氧化物自由基相应值(最大差别不足0.05)。这表明,4-硝基咪唑-*N*-氧化物自由基的1-位和3-位不仅存在较强的互变共振模式,而且二者的稳定性相当,与实验结果吻合[28-29]。众所周知,1-位氮原子上含有取代基的咪唑自由基非常稳定,因此N(1)—NO_2键均裂生成的4-硝基咪唑氧自由基较稳定。由键离解能定义式可知,均裂自由基产物越稳定,键离解能越小。这可能是1,4-DNIO中N—NO_2引发键离解能小的根源。由此可预测,1,4-DNIO不稳定,感度较高。

3.3 撞击感度、静电火花感度和冲击起爆感度

根据Murray等[30]的建议,硝胺炸药的撞击感度H_{50}可按式(1)估算:

$$H_{50} = 0.8849\left[\frac{\sigma_+^2\sigma_-^2}{\sigma_+^2 - \sigma_-^2}\right] - 34.03\left[\frac{\sigma_-^2}{\sigma_+^2}\right]^2 - 43.15 \quad (1)$$

式中,σ_+^2和σ_-^2分别表示表面静电势的正、负方差。

计算结果见表2。Murry等[30]根据式(1)计算得到的无外电场存在下的RDX撞击感度H_{50}值为26 cm,本研究在M06-2X/6-311++G(2d,p)水平上计算的RDX和1,4-DNIO的H_{50}值分别为28 cm和48 cm。可见,1,4-DNIO的撞击感度低于RDX。H_{50}值受外电场强度的影响较大:沿N(3)→O和C(4)—N键轴正方向和N(1)—N键轴负方向的外电场使H_{50}值增大,撞击感度降低;反之,沿N(3)→O和C(4)—N键轴负方向和N(1)—N键轴正方向的外电场使H_{50}值变小,撞击感度升高。该计算结果与N—NO_2在外电场中的引发键强度变化趋势一致,这也证实了N—NO_2是引发键。外电场中H_{50}值的变化量(ΔH_{50})与外电场强度(E)之间存在良好的线性关系(图3)。

根据文献[31],借助式(2)计算了1,4-DNIO在外电场中的静电火花感度E_{ES}:

$$E_{ES} = (-1)^{n1}10.16Q_{nitro} - 1.05n_1n_2E_{LUMO} - 0.20 \quad (2)$$

式中,n_1和n_2分别表示芳香环和取代基的个数,本研究中均取1;Q_{nitro}为N—NO_2引发键的Mulliken硝基电荷;E_{LUMO}为分子前线分子轨道最低空轨道能量。

在B3LYP/6-311G(d,p)理论水平上计算的1,4-DNIO的E_{ES}值为3.66 J,比TNT炸药小[31],表明1,4-DNIO比TNT更敏感。与宋晓书[12]等计算结果类似,外电场对电火花感度影响不大。外电场由-0.010 a.u.变化到0.010 a.u.,静电火花感度的变化值不足0.5 J。

表2 在B3LYP/6-311++G(2d,p)(平滑)和M06-2X/6-311++G(2d,p)(黑体)水平上计算的1,4-DNIO在不同电场大小和方向的部分键离解能(E)、表面静电势统计量(σ_+^2,σ_-^2)、静电火花感度(EES)、撞击感度(H_{50})和冲击起爆压力(ln$p$)

Table 2 Bond dissociation energy (E), statistical quantities of surface electrostatic potentials (σ_+^2,σ_-^2), electric spark sensitivities (E_{ES}), impact sensitivities (H_{50}) and shock initiation pressures (ln$p$) of 1,4-DNIO with different external electric field strengths and orientations at the B3LYP/6-311++G(2d,p) (in flat) and M06-2X/6-311++G(2d,p) (in bold) levels

field	$BDE_{N(3)\rightarrow O}$ /kJ·mol^{-1}	$BDE_{N(1)-N}$ /kJ·mol^{-1}	$BDE_{C(4)-N}$ /kJ·mol^{-1}	E_{LUMO} /a.u.	σ_+^2 /kcal·mol^{-1}	σ_-^2 /kcal·mol^{-1}	E_{ES} /J	H_{50} /cm	ln$p$ /MPa
No field	205.8	54.7	301.1	−0.15384	308.4	78.3	2.30	48	6.78
	189.1	**85.0**	**396.7**	**−0.10739**	**285.3**	**69.6**	**2.07**	**36**	**6.88**
$+0.010_{(N(3)\rightarrow O)}$	171.2	72.8	278.1	−0.17982	352.9	80.1	2.38	68	6.84
	158.8	**99.3**	**373.5**	**−0.12639**	**337.8**	**73.9**	**2.14**	**51**	**6.93**
$+0.008_{(N(3)\rightarrow O)}$	184.1	66.2	285.3	−0.16718	337.0	86.8	2.36	62	6.82
	165.3	**94.5**	**381.0**	**−0.12017**	**318.6**	**75.2**	**2.12**	**45**	**6.91**
$+0.004_{(N(3)\rightarrow O)}$	196.5	58.3	294.5	−0.15872	317.2	82.3	2.32	55	6.79
	180.5	**87.8**	**390.1**	**−0.11236**	**293.8**	**74.6**	**2.09**	**40**	**6.89**
$-0.004_{(N(3)\rightarrow O)}$	213.7	53.5	307.5	−0.15858	302.5	75.3	2.29	44	6.77
	196.8	**83.6**	**404.1**	**−0.11379**	**283.6**	**66.6**	**2.07**	**33**	**6.87**
$-0.008_{(N(3)\rightarrow O)}$	226.8	52.0	318.2	−0.16713	312.3	68.0	2.27	32	6.77
	212.3	**81.8**	**415.3**	**−0.12360**	**280.6**	**59.5**	**2.06**	**29**	**6.86**
$-0.010_{(N(3)\rightarrow O)}$	235.8	51.5	325.2	−0.17138	298.1	62.4	2.25	20	6.76
	227.9	**79.3**	**420.8**	**−0.12289**	**273.6**	**57.3**	**2.05**	**27**	**6.86**
$+0.010_{(N(1)-N)}$	229.5	43.5	322.3	−0.16336	291.6	68.8	2.28	35	6.74
	217.8	**70.2**	**421.7**	**−0.11931**	**276.5**	**55.6**	**2.04**	**17**	**6.82**
$+0.008_{(N(1)-N)}$	222.8	48.1	316.9	−0.16297	290.1	71.9	2.28	39	6.75
	208.2	**77.6**	**417.2**	**−0.11558**	**278.4**	**61.8**	**2.05**	**25**	**6.85**
$+0.004_{(N(1)-N)}$	211.9	52.7	306.2	−0.15427	299.6	76.5	2.29	46	6.77
	196.5	**83.0**	**403.3**	**−0.10956**	**283.7**	**66.2**	**2.06**	**31**	**6.87**
$-0.004_{(N(1)-N)}$	200.1	57.8	295.0	−0.15621	311.5	82.3	2.31	53	6.79
	184.5	**89.2**	**388.1**	**−0.11169**	**288.6**	**74.7**	**2.08**	**44**	**6.89**
$-0.008_{(N1-N)}$	189.9	66.8	281.3	−0.16137	313.7	89.8	2.34	65	6.82
	171.5	**97.2**	**372.7**	**−0.11898**	**298.1**	**80.5**	**2.12**	**52**	**6.92**
$-0.010_{(N(1)-N)}$	180.2	75.7	273.5	−0.16670	319.9	95.6	2.36	74	6.85
	163.7	**104.0**	**360.9**	**−0.12373**	**306.7**	**83.2**	**2.12**	**55**	**6.94**
$+0.010_{(C(4)-N)}$	182.5	66.6	272.3	−0.16577	326.5	92.2	2.35	68	6.82
	167.3	**93.7**	**366.7**	**−0.11826**	**322.3**	**81.5**	**2.11**	**51**	**6.91**
$+0.008_{(C(4)-N)}$	189.7	62.5	280.2	−0.16125	325.2	88.6	2.33	62	6.80
	175.9	**89.1**	**376.5**	**−0.11463**	**302.7**	**76.0**	**2.09**	**45**	**6.89**
$+0.004_{(C(4)-N)}$	200.0	56.1	293.7	−0.15753	318.3	83.5	2.30	55	6.78
	185.2	**85.9**	**389.6**	**−0.10992**	**289.8**	**72.3**	**2.07**	**40**	**6.88**
$-0.004_{(C(4)-N)}$	209.7	53.7	306.5	−0.15927	298.7	75.2	2.30	44	6.77
	196.0	**84.6**	**404.8**	**−0.11123**	**276.5**	**66.8**	**2.06**	**33**	**6.87**
$-0.008_{(C(4)-N)}$	220.5	50.6	318.9	−0.16808	288.5	66.5	2.29	32	6.76
	210.2	**79.3**	**417.2**	**−0.12021**	**265.0**	**63.9**	**2.06**	**29**	**6.86**
$-0.010_{(C(4)-N)}$	227.9	45.1	328.5	−0.17152	283.1	58.1	2.29	20	6.74
	218.3	**72.6**	**429.1**	**−0.12536**	**261.8**	**62.0**	**2.06**	**27**	**6.83**

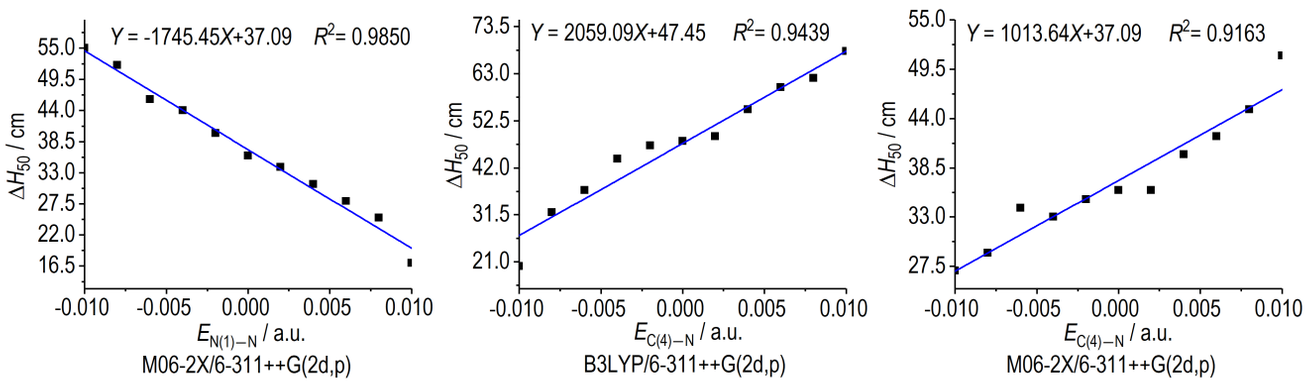

图 3 撞击感度变化值(ΔH_{50})与外电场强度(E)之间的线性关系

Fig. 3 Changes in impact sensitivity values (ΔH_{50}) versus field strengths (E) in different field orientations

冲击起爆压力可用来评价冲击波感度的大小。根据Tan等[25],冲击起爆压力用式(3)计算:

$$\ln p = 6.84\times10^{-4}\mathrm{BDE} + 0.532Q_{\mathrm{nitro}} - 1.28\times10^{-2}\mathrm{BDE}Q_{\mathrm{nitro}} + 2.09 \quad (3)$$

式中,BDE和Q_{nitro}分别取N—NO_2引发键的键离解能和Mulliken硝基电荷。

由表2可知,1,4-DNIO在外电场作用下的冲击起爆压力与季戊四醇四硝酸酯(PETN)(实验值:6.62 MPa[25])接近,而小于HMX(实验值:6.99 MPa和RDX(实验值:7.01 MPa)[25]。因而,1,4-DNIO的冲击波感度接近PETN,而高于HMX和RDX。与静电火花感度类似,外电场对1,4-DNIO冲击起爆压力的影响不大。外电场由−0.010 a.u.变化到0.010 a.u.,冲击起爆压力的变化值低于0.15 MPa。

可以推测,将外电场引入含有N→O配位键分子的含能材料体系,应考虑外电场对炸药撞击感度的影响,可忽略其对静电火花感度和冲击波感度的影响。需要说明的是,本研究中计算得到的外电场中静电火花感度和冲击起爆压力的值是在没考虑外电场与静电场、冲击波耦合作用下的结果。考虑耦合作用下的电火花感度和冲击波感度的理论研究可能成为将来研究的重点,因为耦合是不可避免的。

总之,沿N→O、C—NO_2键轴正方向和N—NO_2负方向的外电场使N→O和C—NO_2键离解能减小、N—NO_2键离解能增大、H_{50}值增大、撞击感度降低;与上述反方向的外电场使N→O和C—NO_2键离解能增大、N—NO_2键离解能减小、H_{50}值减小、撞击感度升高。在外电场作用下,电子在分子(特别是在引发键)的重新分配使分子偶极矩和引发键上成键电子密度发生较大变化,导致引发键离解能和分子的稳定性发生较大变化,引起炸药撞击感度的变化(仅分子水平上)。不同取向的外电场导致电子在分子的重新分配趋势有差异(正负方向外电场引起的结果可能正好相反),从而引起不同的感度变化趋势。

4 结 论

(1)在无电场和外电场作用下,1,4-DNIO中引发键的离解能均遵循以下顺序:$\mathrm{BDE_{N(1)—N}} << \mathrm{BDE_{N(3)\rightarrow O}} < \mathrm{BDE_{C(4)—N}} << \mathrm{BDE_{C(2)—H}}$,因而N—$NO_2$是最可能的引发键,其次是N→O,最后是C—$NO_2$键。

(2)外电场对N—NO_2、N→O、和C—NO_2键强度影响较大,对C—H键性质的影响甚微。引发键键长、AIM电子密度、硝基电荷、键离解能和H_{50}值的变化量与外电场强度之间存在良好的线性关系。

(3)外电场对炸药撞击感度有较大影响,而对电火花感度和冲击起爆压力的度影响不大。可以推测,将外电场引入含有N→O配位键分子的含能材料体系,应考虑外电场对炸药撞击感度的影响,可忽视其对静电火花感度和冲击波感度的影响。

参考文献:

[1] Tasker D. The properties of condensed explosives for electromagnetic energy coupling[J]. *NSWC TR*, 1985: 85-360.

[2] Demske D. The experimental aspects of coupling electrical energy into a dense detonation wave[J]. *NSWC TR*, 1982, 1: 79-143.

[3] Abdulazeem M S, Alhasan A M, Abdulrahmann S. Initiation of solid explosives by laser [J]. *International Journal of Ther-*

mal Sciences, 2011, 50(11): 2117-2121.

[4] Borisenok V A, Mikhailov A S, Bragunets VA. Investigation of the polarization of explosives during impact and the influence of an external electric field on the impact sensitivity of superfine PETN[J]. *Russian Journal of Physical Chemistry B*, 2011, 5(4): 628-639.

[5] Rodzevich A P, Gazenaur E G, Kuzmina LV, et al. The effect of electric field in the explosive sensitivity of silver Azide[J]. *Journal of Physics: Conference Series*, 2017, 830: 012131.

[6] Piehler T, Hummer C, Benjamin R, et al. Preliminary study of coupling electrical energy to detonation reaction zone of primasheet-1000 explosive[C]//27th international symposium on ballistics freiburg. Germany, 2013.

[7] Ren F D, Cao D L, Shi W J. A dynamics prediction of nitromethane→methyl nitrite isomerizatioin in external electric field [J]. *Journal of Molecular Modeling*, 2016, 22: 96

[8] Ren F D, Cao D L, Shi W J, et al. A dynamics prediction of stability for nitromethane in external electric field[J]. *The Royal Society of Chemistry Advances*. 2017, 7: 47063-47072.

[9] Politzer P, Murray J S, Concha M C, et al. Effects of electric fields upon energetic molecules: nitromethane and dimethylnitramine [J]. *Central European Journal Energetic Materials*, 2007, (4): 3-21.

[10] Politzer P, Murray J S, Lane P. Computational determination of effects of electric fields upon "trigger linkages" of prototypical energetic molecules [J]. *International Journal Quantum Chemistry*, 2009, 109: 534-539.

[11] Politzer P, Murray J S. Computed effects of electric fields upon the C—NO_2 and N—NO_2 bonds of nitromethane and dimethylnitramine [J]. *International Journal Quantum Chemistry*, 2009, 109: 3-7.

[12] 宋晓书, 吉世印, 程新路. 几种硝基苯类炸药在外电场作用下的分子特征[J]. 原子与分子物理学报, 2007, 24(5): 916-921.
SONG Xiao-shu, JI Shi-yin, CHENG Xin-lu, et al. The molecular properties of some nitrobenzene explosives in elecric field [J]. *Journal of atomic and molecular physics*, 2007, 24,(5): 916-920.

[13] Lv L, Wei Y, Tao Z Q, et al. Effect of an external electric field on the C—N cleavage reactions in nitromethane and triaminotrinitrobenzene[J]. *Computational and Theoretical Chemistry*, 2017, 1117: 215-219

[14] Tao Z Q, Wang X, Wei Y, et al. A theoretical study of molecular structure, optical properties and bond activation of energetic compound FOX-7 under intense electric fields[J]. *Chemical Physics*, 2016, 483-484: 122-131.

[15] Ren F D, Cao D L, Shi W J, et al. A theoretical prediction of the possible trigger linkage of CH_3NO_2 and NH_2NO_2 in an external electric field[J]. *Journal of Molecular Modeling*, 2015, 21: 145.

[16] Li P, Zhang C, Ren F D, et al. Theoretical insight into the structure and stability of TNT and RDX in external electric field [J]. *India Journal of Pure and Applied Physics*, 2017, 55(8): 604-615.

[17] 冯睿智, 张树海, 任福德, 等. 外电场对不同组分比例的HMX/FOX-7共晶炸药感度影响的理论研究[J]. 化学研究与应用, 2016, 28(4): 479-486.
FENG Rui-zhi, ZHANG Shu-hai, REN Fu-de, et al, Theoretical study on the sensitivity of HMX/FOX-7 cocrystal explosive with different molecular molar ratios in external electric fields [J]. *Chemical Research and Application*, 2016, 28(4): 479-486.

[18] Lobbecke S, Pfeil A, Krause H. Thermal analysis of different nitro furoxans[C]//30th Int. Annu. Conf. of ICT, 1999.

[19] Ravi Surya P, Tewari P. Theoretical investigations on the structure, density, thermodynamic and performance properties of amino-, methyl-, and nitroimidazoles and their *N*-oxides[J]. *Structural Chemistry*, 2012, 23: 1953-1970.

[20] Frisch M J, Trucks G W, Schlegel HB, et. al. Gaussian 09 [CP], *USA: Wallingford CT*, 2009.

[21] Bader RFW. Atoms in molecules[M], *a quantum theory*, *Oxford University Press*, *Oxford*, *UK*, 1990.

[22] Murray JS, Politzer P. The electrostatic potential: an overview [J]. *WIREs Computional Molecular Science 2011*, (1): 153-163

[23] Zhang C Y, Shu Y J, Huang Y G, et al. Investigation of correlation between impact sensitivities and Nitro group charges in Nitro compounds [J]. *Journal Physical Chemistry B*, 2005, 109: 8978-8982.

[24] Li J S. A quantitative relationship for the shock sensitivities of energetic compounds based on *X*—NO_2(*X*=C,N,O) bond dissociation energy [J]. *Journal of Hazardous Materials*, 2010, 180: 768-772.

[25] Tan B S, Long X P, Peng R F, et al. Two important factors influencing shock sensitivity of nitro compounds: Bond dissociation energy of *X*—NO_2(*X*=C, N, O) and Mulliken charges of nitro group[J]. *Journal of Hazardous Materials*, 2010, 183: 908-912.

[26] Bulusu S N. Chemistry and physics of energetic materials [M]. *Kluwer Academic Publishers* , 1990.

[27] Schleyer PvR, Maerker C, Dransfeld A, et al. Nucleus-independent chemical shifts: A simple and efficient aromaticity probe[J]. *Journal of the American Chemical Society*, 1996, 118: 6317-6318.

[28] Bracuti A J, Molecular structure of a new potential propellant oxidize 4,5-dinitroimdazole[J]. *Journal of Chemical Crystallography*, 1996, 28(5): 367-371.

[29] Wang J, Dong H, Zhang X Y, et al. Synthesis, Thermal stability and sensitivity of 2,4-dinitroimdazole[J]. *Chinese Journal of Energetic Materials*, 2010, 18(6): 728-729.

[30] Murry J S, Lane P, Politzer P. Effects of strongly electron-attracting components on molecular surface electrostatic potentials application to predicting impact sensitivities of energetic molecules[J]. *Molecular Physics*, 1998, 93(2): 187-194.

[31] Zhi C, Cheng X. The correlation between electric spark sensitivity of polynitroaromatic compounds and their molecular electronic properties[J]. *Propellants Explosives Pyrotechnics*, 2010, 35: 555-560.

Theoretical Prediction of the Sensitivity of 1,4-Dinitroimidazole-*N*-oxide in the External Electric Fields

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Abstract: In order to explore the variation rule of explosives′ sensitivity in the external electric field, the bond lengths, nitro charges, bond dissociation energies of the potential trigger linkages and the impact sensitivities, electrostatic spark sensitivities as well as shock initiation pressures of the 1,4-dinitroimidazole-*N*-oxide (1,4-DNIO) explosive were investigated by the B3LYP/6-311++G(2d,p) and M06-2X/6-311++G(2d,p) levels of theory. Results show that the N—NO_2 bond is the most likely trigger linkage in the initiation reaction of explosive, followed by N→O, and finally the C—NO_2 bond in the external electric fields and the absence of the electric fields. Under the external electric fields along the positive directions of the N→O and C—NO_2 bond axes as well as the negative direction of the N—NO_2 bond axis, the dissociation energies of the N→O and C—NO_2 bonds are decreased, while those of N—NO_2 bond are increased, leading to the increases of the H_{50} values and thus the decreases of the impact sensitivities. The opposite conclusion is drawn when the explosives are in the external electric fields with the reverse directions against the above cases. The changes in the bond lengths (ΔR), electron density values ($\Delta\rho$), nitro charges (ΔQ), bond dissociation energy (ΔBDEs) of the trigger linkages and thoes in the impact sensitivities (ΔH_{50}) show good linear relationships with the external electric field strengths, respectively. In most cases, the values of correlation coefficient R^2 are larger than 0.9500. The external electric fields have little effect on the electrostatic spark sensitivities or shock initiation pressures, accompanied by the variations lower than 0.5 J and 0.15MPa with the field strengths from －0.0010 a.u. to 0.0010 a.u., respectively.

Key words: 1,4-dinitroimidazole-*N*-oxide (1,4-DNIO); sensitivity; external electric field; density functional theory; surface electrostatic potential

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