



## Effects of Electric Fields Upon Energetic Molecules: Nitromethane and Dimethylnitramine

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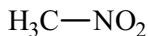
**Abstract:** We have investigated computationally (B3PW91/6-31G\*\*) the effects of electric fields upon certain properties – dipole moments, energies, geometries and electrostatic potentials – of two prototypical energetic molecules, nitromethane and dimethylnitramine. Fields of various strengths and in different directions were considered. The stronger fields significantly polarized the molecular charge distributions, especially when applied parallel to the C–NO<sub>2</sub> and the N–NO<sub>2</sub> bonds. These directions correspond to the principal polarities of the ground-state molecules, which these parallel fields either reinforce or counteract. With respect to geometries, the changes are primarily conformational, e.g. rotation of the methyl groups or inversion of the pyramidal nitrogen in (H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>.

**Keywords:** electric fields, electrostatic potentials, dipole moments, nitromethane, dimethylnitramine

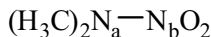
## Introduction

Our objective in this study has been to determine computationally how two prototypical energetic molecules, nitromethane (**1**) and dimethylnitramine (**2**), respond to external electric fields. We will look at how the fields affect the molecules' geometries, energies, dipole moments and electrostatic potentials. Of particular interest will be their influence upon the C–NO<sub>2</sub> and the N–NO<sub>2</sub>

bonds. In the context of explosives, these are often viewed as “trigger linkages”, the rupture of which is believed to be a key step in the initiation of detonation [1-4]. The properties of C–NO<sub>2</sub> and N–NO<sub>2</sub> bonds have indeed been linked to the sensitivities of energetic compounds toward impact and shock [4-9].



1



2

## Procedure

Each molecular geometry was optimized and properties computed at the density functional B3PW91/6-31G\*\* level in the presence of electric fields of different strengths and directions. The Gaussian 03 code was used [10]. In each instance, the molecular electrostatic potential was calculated and analyzed on the molecular surface defined, following Bader *et al* [11], by the 0.001 electrons/bohr<sup>3</sup> contour of the molecule’s electronic density  $\rho(\mathbf{r})$ . The Hardsurf program was utilized for this purpose [12].

The electrostatic potential  $V(\mathbf{r})$  that is created by the nuclei and electrons of a molecule in the surrounding space is given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

where  $Z_A$  is the charge on nucleus A, located at  $\mathbf{R}_A$ .  $V(\mathbf{r})$  is a physical observable, which can be obtained experimentally by diffraction techniques [13, 14] as well as computationally. When evaluated on a molecular surface,  $V(\mathbf{r})$  is labeled  $V_s(\mathbf{r})$ . We customarily characterize  $V_s(\mathbf{r})$  by means of several statistically defined quantities [15]; in the present work, these have been the local maxima  $V_{s,\max}$  and minima  $V_{s,\min}$  (i.e. the most positive and most negative values of the potential) and the positive and negative variances,  $\sigma_+^2$  and  $\sigma_-^2$ :

$$\sigma_+^2 = \frac{1}{m} \sum_{i=1}^m [V_s^+(\mathbf{r}_i) - \bar{V}_s^+]^2 \quad (2)$$

$$\sigma_-^2 = \frac{1}{n} \sum_{j=1}^n [V_s^-(\mathbf{r}_j) - \bar{V}_s^-]^2 \quad (3)$$

In eqs. (2) and (3),  $\bar{V}_s^+$  and  $\bar{V}_s^-$  are the averages of the positive and negative values of  $V_s(\mathbf{r})$ ,  $V_s^+(\mathbf{r}_i)$  and  $V_s^-(\mathbf{r}_j)$ , summed up over the  $m$  positive and  $n$  negative points on the surface. The variances  $\sigma_+^2$  and  $\sigma_-^2$  are measures of the variabilities of the positive and negative surface potentials; they emphasize the respective extremes, the local maxima and minima, because of the terms being squared.

## Results and Discussion

### Dipole Moments

The first-order response of a molecule's charge distribution to an external electric field  $\boldsymbol{\varepsilon}$  is governed by the molecule's polarizability  $\boldsymbol{\alpha}$ . The resulting change in its dipole moment  $\boldsymbol{\mu}$  is

$$\boldsymbol{\mu}(\boldsymbol{\varepsilon}) - \boldsymbol{\mu}(0) = \boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon} \quad (4)$$

The polarizability is a second-rank nine-component tensor, which can be expressed as a symmetric 3 x 3 matrix [16]; in a Cartesian frame of reference,

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix} \quad (5)$$

Eq. (5) means that an electric field in, for example, the  $\pm x$  direction may affect not only the  $x$  component of  $\boldsymbol{\mu}$ , but the  $y$  and  $z$  as well, via  $\alpha_{xy}$  and  $\alpha_{xz}$ .

What is reported in the literature is often the scalar or average polarizability  $\alpha$ . This is defined in terms of the diagonal elements of the matrix in eq. (5):

$$\alpha = \langle \boldsymbol{\alpha} \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (6)$$

In Tables 1 and 2 are reported, for nitromethane and for dimethylnitramine, the computed dipole moments and their components in the presence of electric fields of various strengths and directions. In  $\text{H}_3\text{C}-\text{NO}_2$ , the carbon is at the origin and the nitrogen is on the  $+z$  axis; the  $x$  axis is in the  $\text{C}-\text{NO}_2$  plane, the  $y$  is perpendicular to it. In  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$ ,  $\text{N}_a$  (the nitrogen bearing the methyl groups) is at the origin, with  $\text{N}_b$  on the  $+z$  axis. The  $x$  axis is in the  $\text{N}-\text{NO}_2$  plane and the  $y$  is perpendicular to it.

**Table 1.** Effects of electric fields on dipole moment of nitromethane,  $\text{H}_3\text{C}-\text{NO}_2$ . Calculations at B3PW91/6-31G\*\* level<sup>a</sup>

Field, $\pm x$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	1.90	0.95	0.10	0.01	-0.08	-0.92	-1.90
<i>y</i> component	0.00	-0.01	-0.01	-0.01	-0.01	-0.01	0.00
<i>z</i> component	-3.50	-3.50	-3.49	-3.49	-3.49	-3.47	-3.50
Total dipole moment	-3.98	-3.62	-3.49	-3.49	-3.49	-3.59	-3.98
Field, $\pm y$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	0.03	0.00	0.01	0.01	0.00	0.00	0.03
<i>y</i> component	1.01	0.52	0.04	-0.01	-0.07	-0.52	-1.01
<i>z</i> component	-3.52	-3.50	-3.49	-3.49	-3.49	-3.50	-3.52
Total dipole moment	-3.66	-3.54	-3.49	-3.49	-3.49	-3.54	-3.66
Field, $\pm z$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	-0.02	0.00	0.01	0.01	0.01	0.02	0.00
<i>y</i> component	0.00	-0.01	-0.01	-0.01	-0.01	-0.01	-0.04
<i>z</i> component	-1.98	-2.74	-3.41	-3.49	-3.56	-4.24	-5.00
Total dipole moment	-1.98	-2.74	-3.41	-3.49	-3.56	-4.24	-5.00

<sup>a</sup> Dipole moments are in Debyes. The directions are from negative to positive.<sup>b</sup> Carbon is at origin, nitrogen is on  $\pm z$  axis, *x*-axis is in C-NO<sub>2</sub> plane, *y*-axis is perpendicular to C-NO<sub>2</sub> plane.<sup>c</sup> 1 au = 51.42 V/Å.**Table 2.** Effects of electric fields on dipole moment of dimethylnitramine,  $(\text{H}_3\text{C})_2\text{N}_a-\text{N}_b\text{O}_2$ . Calculations at B3PW91/6-31G\*\* level<sup>a</sup>

Field, $\pm x$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	2.99	1.48	0.14	-0.01	-0.16	-1.50	-3.02
<i>y</i> component	0.75	0.75	0.77	0.77	0.77	0.80	0.84
<i>z</i> component	-4.41	-4.43	-4.43	-4.43	-4.42	-4.41	-4.36
Total dipole moment	-5.38	-4.73	-4.50	-4.49	-4.49	-4.72	-5.37
Field, $\pm y$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	0.00	-0.02	-0.01	-0.01	-0.01	-0.02	0.00
<i>y</i> component	2.99	1.96	0.90	0.77	0.63	-1.96	-2.99
<i>z</i> component	-4.25	-4.27	-4.41	-4.43	-4.45	-4.27	-4.25
Total dipole moment	-5.19	-4.70	-4.50	-4.49	-4.49	-4.69	-5.19
Field, $\pm z$ direction, <sup>b</sup> au <sup>c</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
<i>x</i> component	-0.02	-0.02	-0.01	-0.01	-0.01	0.00	0.00
<i>y</i> component	0.98	0.95	0.79	0.77	0.74	-0.01	-0.01
<i>z</i> component	-0.88	-2.64	-4.25	-4.43	-4.61	-6.29	-7.83
Total dipole moment	-1.31	-2.81	-4.32	-4.49	-4.67	-6.29	-7.83

<sup>a</sup> Dipole moments are in Debyes. The directions are from negative to positive.<sup>b</sup> N<sub>a</sub> (nitrogen bearing the methyl groups) is at origin, N<sub>b</sub> is on  $\pm z$  axis; *x*-axis is in N-NO<sub>2</sub> plane, *y*-axis is perpendicular to N-NO<sub>2</sub> plane.<sup>c</sup> 1 au = 51.42 V/Å.

Since  $\mu$  is a vector, its magnitude is

$$|\mu| = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (7)$$

The direction of a dipole moment is taken to be from negative to positive.

For  $\text{H}_3\text{C}-\text{NO}_2$  in the absence of a field,  $\mu_x$  and  $\mu_y$  are found to be essentially zero (Table 1); the polarity is parallel to the C–N bond:  $|\mu| = \mu_z = -3.49$  D. The minus sign means, in the present coordinate system, that the  $\text{CH}_3$  portion of the molecule is the positive end of the dipole. This is of course fully consistent with the strongly electron-withdrawing nature of the  $\text{NO}_2$  group [17]. Our predicted magnitude of  $\mu$  for the ground-state  $\text{H}_3\text{C}-\text{NO}_2$  molecule, 3.49 D, is in very good agreement with the experimental 3.46 D [18].

In the case of  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$  at zero field,  $\mu_x \approx 0$  but we do obtain a  $y$  component,  $\mu_y = 0.77$  D (Table 2). This is due to the two carbons being 0.30–0.4 Å above the N– $\text{NO}_2$  plane, in the  $+y$  direction. The primary polarity is parallel to the N–N bond,  $\mu_z = -4.43$  D. The overall dipole moment is thus  $-4.49$  D, with the  $\text{NO}_2$  group again being the negative end.

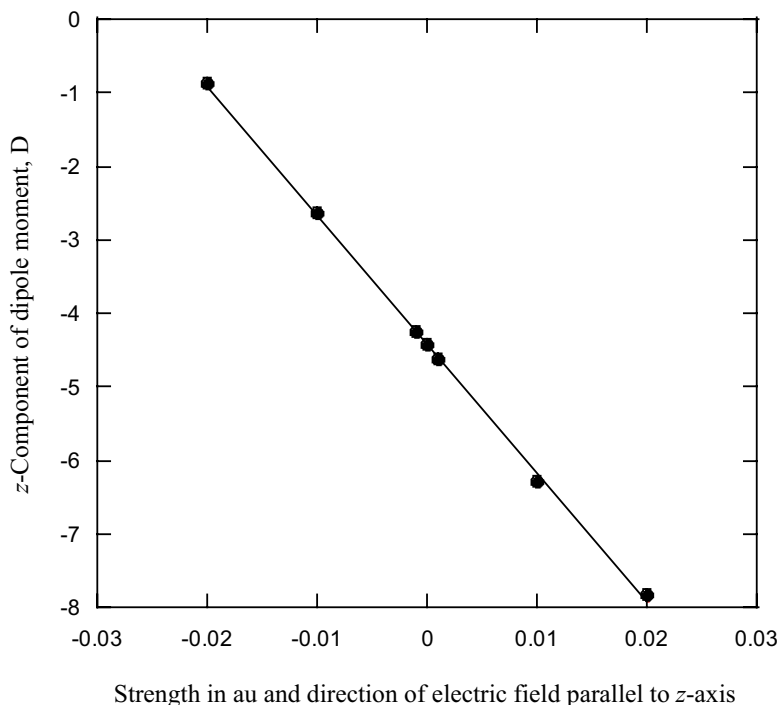
When an electric field is imposed parallel to the  $x$ ,  $y$  or  $z$  axes of  $\text{H}_3\text{C}-\text{NO}_2$  and  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$  (using the present coordinate systems), its effect upon their dipole moments is seen primarily in the corresponding component of  $\mu$  (Tables 1 and 2). Thus a field in the positive or negative  $x$  direction may change  $\mu_x$  quite significantly (depending upon its strength), but  $\mu_y$  and  $\mu_z$  are essentially unaffected. This indicates that the off-diagonal elements in the  $\alpha$ -matrices of  $\text{H}_3\text{C}-\text{NO}_2$  and  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$ , eq. (5), are mostly very small, especially for  $\text{H}_3\text{C}-\text{NO}_2$ . The main exception to this is  $\alpha_{yz}$  of  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$ , as evidenced by the fact that  $\mu_y$  changes from 0.98 D to  $-0.01$  D for fields between  $-0.020$  and  $+0.020$  au parallel to the  $z$  axis (Table 2).

As predicted by eq. (4), each component of  $\mu$  varies linearly with the magnitude of a field in that direction; for example,

$$\mu_z(\epsilon) = \mu_z(0) + \alpha_{zz}\epsilon \quad (8)$$

when  $\epsilon$  is parallel to the  $z$ -axis (see Figure 1). In most instances, we obtained

$R^2 > 0.999$  for field strengths of  $-0.020$  to  $+0.020$  au. The greatest deviation from linearity,  $R^2 = 0.949$ , is found for  $\mu_y$  of  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$ . This can be understood in terms of the changes in geometry that occur with  $\pm y$  fields, to be examined in the next section.



**Figure 1.**  $z$ -Component of dimethylnitramine dipole moment, in D, plotted against strength of  $\pm z$  external electric field, in au  $R^2 = 0.9992$ .

From relationships such as eq. (8), we are able to estimate  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$  for each molecule, and hence its scalar polarizability via eq. (6). The results are  $\alpha = 4.3 \text{ \AA}^3$  for  $\text{H}_3\text{C}-\text{NO}_2$  and  $\alpha = 8.9 \text{ \AA}^3$  for  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$ . While we are not aware of any recent experimental measurements, the value for  $\text{H}_3\text{C}-\text{NO}_2$  is in good agreement with a prediction of  $4.8 \text{ \AA}^3$  based on group volumes and local ionization energies [19].

Due to the approximate symmetry of  $\text{H}_3\text{C}-\text{NO}_2$ , the changes in  $\mu_x$  for fields in both directions parallel to the  $x$  axis are quite similar in magnitude (but opposite in sign); this is true as well for  $\mu_y$  and fields parallel to the  $y$  axis. The same can be said for  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$  with regard to  $\mu_x$ , but for  $\mu_y$  the situation is complicated somewhat by the fact that the carbons in  $(\text{H}_3\text{C})_2\text{N}-\text{NO}_2$  are not coplanar with the  $\text{N}-\text{NO}_2$  portion of the molecule. This will be discussed further in the next section.

Most interesting for both molecules, however, are the effects of fields in the  $\pm z$  directions upon  $\mu_z$ , which is generally the dominant contribution to the overall dipole moment. As the external field becomes stronger in the  $+z$  direction, there

is a marked increase in the magnitudes of both  $\mu_z$  and  $\mu$  for each molecule, the  $\text{NO}_2$  portions becoming more negative. Fields in the  $-z$  direction correspondingly reduce the polarities of the molecules. A more detailed picture will emerge from the molecular surface electrostatic potentials.

### Energies and Geometries

Tables 3 and 4 show how each molecule's energy and key bond lengths are influenced by external electric fields. The effects of fields parallel to the  $x$  and  $y$  axes (i.e. perpendicular to the  $\text{C}-\text{NO}_2$  and  $\text{N}-\text{NO}_2$  bonds) are mostly rather small for  $|\epsilon| \leq 0.010$  au, and even for  $|\epsilon| = 0.020$  au, they show definite patterns relative to zero field, which again reflect the molecules' approximate symmetries. The energies are nearly always lowered, and by essentially the same amounts for fields in the positive and negative directions. Fields in the  $+x$  direction lengthen one  $\text{N}-\text{O}$  (or  $\text{C}-\text{N}$ ) bond and shorten the other; those in the  $-x$  direction do the opposite. This is due to the differences in the relative orientations of the fields and the bond polarities.

**Table 3.** Effects of electric fields on molecular energy and key bond lengths of nitromethane,  $\text{H}_3\text{C}-\text{NO}_2$ . All calculations at B3PW91/6-31G\*\* level

Field, $\pm x$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	-4.7	-1.2	0.0	0.0	0.0	-1.1	-4.7
C-N bond length, Å	1.492	1.492	1.492	1.492	1.492	1.492	1.492
N-O bond lengths, Å	1.242 1.205	1.231 1.213	1.222 1.221	1.222	1.221 1.222	1.213 1.232	1.205 1.242
Field, $\pm y$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	-2.6	-0.7	0.0	0.0	0.0	-0.7	-2.6
C-N bond length, Å	1.491	1.492	1.492	1.492	1.492	1.492	1.492
N-O bond lengths, Å	1.221 1.222	1.222	1.222 1.221	1.222	1.222	1.222	1.221 1.222
Field, $\pm z$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	+13.5	+7.7	+0.9	0.0	-0.9	-9.5	-20.9
C-N bond length, Å	1.504	1.496	1.492	1.492	1.492	1.490	1.490
N-O bond lengths, Å	1.215 1.216	1.218 1.219	1.221 1.222	1.222	1.222	1.224 1.225	1.228

<sup>a</sup> Carbon is at origin, nitrogen is on  $+z$  axis,  $x$ -axis is in  $\text{C}-\text{NO}_2$  plane,  $y$ -axis is perpendicular to  $\text{C}-\text{NO}_2$  plane.

<sup>b</sup> 1 au = 51.42 V/Å.

**Table 4.** Effects of electric fields on molecular energy and key bond lengths of dimethylnitramine,  $(\text{H}_3\text{C})_2\text{N}_a\text{-N}_b\text{O}_2$ . All calculations at B3PW91/6-31G\*\* level

Field, $\pm x$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	-7.3	-1.8	0.0	0.0	0.0	-1.9	-7.4
C-N bond lengths, Å	1.468 1.440	1.459 1.445	1.452 1.450	1.451	1.450 1.452	1.445 1.459	1.442 1.469
N-N bond length, Å	1.376	1.375	1.376	1.376	1.376	1.377	1.380
N-O bond lengths, Å	1.248 1.209	1.237 1.217	1.227 1.226	1.227	1.226 1.228	1.217 1.236	1.209 1.247
Field, $\pm y$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	-9.5	-3.4	-0.2	0.0	+0.2	-3.4	-9.5
C-N bond lengths, Å	1.471 1.470	1.461	1.452	1.451	1.450	1.461	1.471 1.470
N-N bond length, Å	1.398	1.390	1.377	1.376	1.375	1.390	1.398
N-O bond lengths, Å	1.226 1.224	1.226 1.225	1.227 1.226	1.227	1.227 1.226	1.226 1.225	1.226 1.224
Field, $\pm z$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
Relative molecular energy, kcal/mole	+13.1	+8.7	+1.1	0.0	-1.1	-13.2	-30.6
C-N bond lengths, Å	1.449	1.451	1.451	1.451	1.451	1.453	1.458
N-N bond length, Å	1.455	1.412	1.379	1.376	1.372	1.344	1.332
N-O bond lengths, Å	1.210	1.218	1.226	1.227	1.227	1.237	1.244

<sup>a</sup>  $\text{N}_a$  (nitrogen bearing the methyl groups) is at origin,  $\text{N}_b$  is on  $+z$  axis;  $x$ -axis is in  $\text{N-NO}_2$  plane,  $y$ -axis is perpendicular to  $\text{N-NO}_2$  plane.

<sup>b</sup> 1 au = 51.42 V/Å.

In the ground-state  $(\text{H}_3\text{C})_2\text{N-NO}_2$  molecule, the nitrogen bearing the methyls is somewhat pyramidal, and so the carbons are out of the  $\text{N-NO}_2$  plane, by 0.3-0.4 Å in the  $+y$  direction. This accounts for  $\mu_y$  being +0.77 D (Table 2), and it is only slightly affected by weak fields ( $\pm 0.001$  au), in either  $y$  direction. However fields of +0.010 and +0.020 au are able to move the carbons to the other side of the  $\text{N-NO}_2$  plane, producing  $\mu_y = -1.96$  D and  $-2.99$  D. Remarkably, the carbons are now at almost exactly the same distances from the plane in the  $-y$  direction as they are in the  $+y$  for fields of  $-0.010$  and  $-0.020$  au; for the latter two cases,  $\mu_y = +1.96$  D and  $+2.99$  D.

Nevertheless it is again the fields parallel to the  $z$  axes (i.e parallel to the  $\text{C-NO}_2$  and  $\text{N-NO}_2$  bonds) that have the most notable consequences. As the field is increased in the  $+z$  direction, which has already been seen to produce



a higher level of polarity in each molecule (Tables 1 and 2), their energies are lowered quite significantly and the C–NO<sub>2</sub> and N–NO<sub>2</sub> bond lengths decrease. The reverse occurs for fields in the  $-z$  direction. The effects tend to be greater for (H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>; the change in energy reaches  $-30.6$  kcal/mole for a  $+z$  field of  $+0.020$  au, while the N–NO<sub>2</sub> distance ranges from 1.332 Å for  $+0.020$  au to 1.455 Å for  $-0.020$  au. The latter may reflect the fact that N–NO<sub>2</sub> bonds tend to be weaker than C–NO<sub>2</sub> [20, 21]. The  $+0.010$  and  $+0.020$  au fields in the  $+z$  direction in (H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub> also cause the carbons to move into the N–NO<sub>2</sub> plane, which explains why  $\mu_y$  suddenly drops to essentially zero (Table 2). Finally, the electric fields, especially the stronger ones, cause some rotation of the methyl groups.

## Electrostatic Potentials

### *Nitromethane*



**Figure 2.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of ground-state nitromethane (H<sub>3</sub>C–NO<sub>2</sub>). The hydrogens are at the top, the oxygens at the bottom. Color ranges, in kcal/mole, are: purple, more negative than 0; blue, between 0 and 15; green, between 15 and 23; yellow, between 23 and 25; red, more positive than 25.

In Figure 2 is presented the computed electrostatic potential  $V_s(\mathbf{r})$  on the molecular surface of ground-state nitromethane, taken to be the 0.001 electrons/bohr<sup>3</sup> contour of its electronic density. The key features of  $V_s(\mathbf{r})$ , for our present purposes, are the strongly negative potentials of the oxygens, which reach extrema of  $V_{s,\min} = -31$  kcal/mole, the positive regions around the hydrogens, with  $V_{s,\max}$  of  $+27$  to  $+30$  kcal/mole, and a weaker but very interesting local maximum of  $+24$  kcal/mole above the C–NO<sub>2</sub> bond (Table 5). Such local  $V_{s,\max}$

are not associated with chemical bonds in general, but they have been found for C–NO<sub>2</sub> bonds in nitroaromatics, nitroheterocycles and nitroalkanes [7, 22, 23]. These  $V_{S,max}$  correlate to some extent, inversely, with the C–NO<sub>2</sub> bond energies [7, 23], and have been linked to impact sensitivities. Such positive buildups above C–NO<sub>2</sub> bonds have also been demonstrated to provide a path for the initial approach of nucleophiles [24, 25].

**Table 5.** Effects of electric fields on molecular surface electrostatic potential of nitromethane, H<sub>3</sub>C–NO<sub>2</sub>. Calculations at B3PW91/6-31G\*\* level

Field, $\pm x$ direction, <sup>a</sup> au <sup>b</sup>	−0.020	−0.010	−0.001	0.0	+0.001	+0.010	+0.020
$\sigma_+^2$ , (kcal/mole) <sup>2</sup>	111.3	68.3	50.4	49.8	49.0	57.1	110.8
$\sigma_-^2$ , (kcal/mole) <sup>2</sup>	151.8	83.0	60.3	59.8	60.2	86.3	152.7
$V_{S,min}$ , kcal/mole oxygens	−40	−35	−31,−31	−31,−31	−31,−30	−35	−40
$V_{S,max}$ , kcal/mole C–NO <sub>2</sub> bond hydrogens	---	---	24	24	24	25	---
	37,37	33,33	30,29,26	30,29,27	29,29,27	33,27,25	37,37
Field, $\pm y$ direction, <sup>a</sup> au <sup>b</sup>	−0.020	−0.010	−0.001	0.0	+0.001	+0.010	+0.020
$\sigma_+^2$ , (kcal/mole) <sup>2</sup>	107.3	66.8	49.6	49.8	50.4	66.7	107.4
$\sigma_-^2$ , (kcal/mole) <sup>2</sup>	64.6	60.8	59.7	59.8	60.1	61.4	64.6
$V_{S,min}$ , kcal/mole oxygens	−32,−31	−31,−31	−31,−31	−31,−31	−31,−31	−31,−31	−32,−31
$V_{S,max}$ , kcal/mole C–NO <sub>2</sub> bond hydrogens	12	18	24	24	23	18	12
	44	37,25,25	29,29,27	30,29,27	31,27,27	37,25,25	44
Field, $\pm z$ direction, <sup>a</sup> au <sup>b</sup>	−0.020	−0.010	−0.001	0.0	+0.001	+0.010	+0.020
$\sigma_+^2$ , (kcal/mole) <sup>2</sup>	23.9	31.5	48.0	49.8	51.9	76.5	112.8
$\sigma_-^2$ , (kcal/mole) <sup>2</sup>	23.4	38.9	57.4	59.8	62.0	85.4	117.7
$V_{S,min}$ , kcal/mole oxygens	−20,−19	−26,−25	−30,−30	−31,−31	−32,−31	−37,−36	−43,−43
$V_{S,max}$ , kcal/mole C–NO <sub>2</sub> bond hydrogens	23	24	24	24	24	---	---
	21,20,17	25,24,22	29,28,26	30,29,27	30,30,27	35,34,32	41

<sup>a</sup> Carbon is at origin, nitrogen is on  $+z$  axis,  $x$ -axis is in C–NO<sub>2</sub> plane,  $y$ -axis is perpendicular to C–NO<sub>2</sub> plane.

<sup>b</sup> 1 au = 51.42 V/Å.

In Table 5 are the values of these properties under the influence of electric fields parallel to the  $x$ ,  $y$  and  $z$  axes. Also included are the positive and negative variances of  $V_S(\mathbf{r})$ ,  $\sigma_+^2$  and  $\sigma_-^2$ . These indicate the overall variabilities of the positive and negative surface potentials in each case. Their magnitudes for the ground state,  $\sigma_+^2 = 49.8$  (kcal/mole)<sup>2</sup> and  $\sigma_-^2 = 59.8$  (kcal/mole)<sup>2</sup> (B3PW91/6-31G\*\*), are fairly representative for organic molecules. Typically  $\sigma_-^2 > \sigma_+^2$ , but this may

be reversed when there are several strongly electron-attracting groups in the molecule, e.g.  $\text{NO}_2$  [26].

In general, the fields in the  $\pm x$ ,  $\pm y$  and  $\pm z$  directions increase the polarization of the molecule. This overall result was already evident in the dipole moments in Table 1, but Table 5 shows more details. The effects are rather minor for the weak fields ( $\pm 0.001$  au) but can be quite substantial for the stronger ones. Thus, whereas each oxygen has a distinct negative region and  $V_{S,\min}$  in the ground state, and each hydrogen a positive region and a  $V_{S,\max}$ , the fields sometimes cause a merging of the negative regions, or the positive ones, resulting in just one  $V_{S,\min}$  and/or only one or two  $V_{S,\max}$ .

For example, the two oxygens have  $V_{S,\min} = -31$  kcal/mole in the ground state. However fields in the  $\pm x$  directions cause one oxygen to become much more negative, reaching  $-40$  kcal/mole, while the other does not anymore have a  $V_{S,\min}$ ; its negative potential has blended together with that of its neighbor. Similarly, while the three hydrogens initially all have  $V_{S,\max}$  between  $+27$  and  $+30$  kcal/mole, two of them eventually become more positive in the presence of fields in the  $\pm x$  directions and the third no longer has a  $V_{S,\max}$ . For  $y$  fields of  $\pm 0.020$  au, just one hydrogen has an identifiable (and stronger)  $V_{S,\max}$ .

As was observed in Tables 1 and 3, the changes induced by  $\pm x$  and  $\pm y$  fields are symmetric with respect to the ground state (Table 5). However whether a given atom becomes more positive or more negative depends upon the direction of the field.

The  $V_{S,\max}$  above the C- $\text{NO}_2$  bond varies significantly in magnitude only for the  $\pm y$  fields, but it tends to shift its position. In the ground state, it is directly over the C-N axis, but  $\pm x$  fields push it to one side or the other. For the stronger  $\pm x$  fields, it actually merges with the positive regions of the hydrogens and can no longer be separately identified. On the other hand,  $\pm y$  fields move the C- $\text{NO}_2$   $V_{S,\max}$  up or down, perpendicularly to the C-N axis and the C- $\text{NO}_2$  plane. Thus its value on the  $0.001$  electrons/bohr<sup>3</sup> molecular surface diminishes.

All of these field-induced consequences are summarized in the variances,  $\sigma_+^2$  and  $\sigma_-^2$  (Table 5). These increase with the strengths of the fields, consistent with the higher degrees of polarization. Note that the strong  $\pm y$  fields produce the unusual situation that  $\sigma_+^2 > \sigma_-^2$ .

Both the highest and the lowest levels of polarization result from fields in the  $\pm z$  directions, i.e. parallel to the C- $\text{NO}_2$  bond. For a field of  $+0.020$  au, the oxygens become very negative,  $V_{S,\min} = -43$  kcal/mole, and the hydrogens very positive, reaching  $+41$  kcal/mole. No C- $\text{NO}_2$  bond  $V_{S,\max}$  can be distinguished in the large, strongly positive potential of the hydrogens (Figure 3). The variances,  $\sigma_+^2$  and  $\sigma_-^2$ , are twice as large as in the ground state. Figure 3 shows that the surface

potential has the appearance that would be expected for an ionic molecule or perhaps a zwitterion [27]. The dipole moment is the largest observed for any of the fields investigated,  $\mu = -5.0$  D (Table 1).



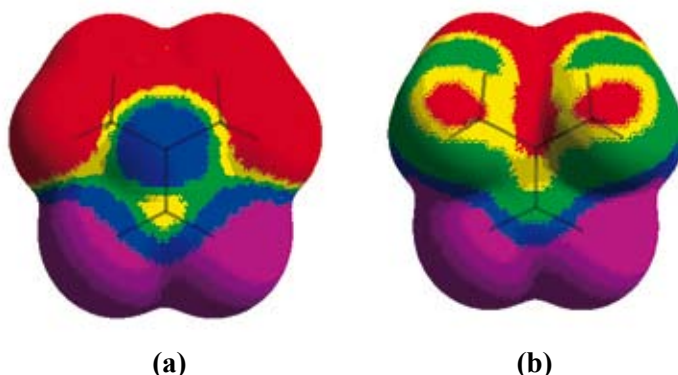
**Figure 3.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of nitromethane (H<sub>3</sub>C–NO<sub>2</sub>) in the presence of an electric field in the +z direction with a strength of 0.020 au. The hydrogens are at the top, the oxygens at the bottom. Color ranges, in kcal/mole, are: purple, more negative than –20; blue, between –20 and 0; green, between 0 and 20; yellow, between 20 and 30; red, more positive than 30.



**Figure 4.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of nitromethane (H<sub>3</sub>C–NO<sub>2</sub>) in the presence of an electric field in the –z direction with a strength of 0.020 au. The hydrogens are at the top, the oxygens at the bottom. Color ranges, in kcal/mole, are: purple, more negative than –20; blue, between –20 and 0; green, between 0 and 20; yellow, between 20 and 30; red, more positive than 30.

The other extreme is observed with strong fields in the  $-z$  direction (Figure 4). The oxygen  $V_{S,\min}$  decrease in magnitude to  $-19$  and  $-20$  kcal/mole, and the hydrogen  $V_{S,\max}$  to between  $+17$  and  $+21$  kcal/mole. The  $V_{S,\max}$  over the C-NO<sub>2</sub> bond is clearly visible. The values of  $\sigma_z^2$  and  $\sigma_z^2$  are diminished, indicating a relatively weak surface potential of little variability, and this is indeed what is seen in Figure 4. The level of polarization, and hence the dipole moment (Table 1), is much below that of the ground state.

### *Dimethylnitramine*



**Figure 5.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of ground-state dimethylnitramine [(H<sub>3</sub>C)<sub>2</sub>N-NO<sub>2</sub>]. The hydrogens are at the top, the oxygens at the bottom. Two views are shown: (a) side of molecule with nitrogen lone pair; color ranges, in kcal/mole, are: purple, more negative than  $-10$ ; blue, between  $-10$  and  $0$ ; green, between  $0$  and  $3$ ; yellow, between  $3$  and  $6$ ; red, more positive than  $6$ ; (b) side of molecule without lone pair; color ranges, in kcal/mole, are: purple, more negative than  $0$ ; blue, between  $0$  and  $10$ ; green, between  $10$  and  $18$ ; yellow, between  $18$  and  $19$ ; red, more positive than  $19$ .

The molecular surface electrostatic potential of ground-state dimethylnitramine, Figure 5, again has strongly negative oxygen regions, with two  $V_{S,\min}$  of  $-36$  kcal/mole, and positive ones around the hydrogens, the  $V_{S,\max}$  being between  $+17$  and  $+29$  kcal/mole (Table 6). There are also two new features. Since N<sub>a</sub>, the nitrogen bearing the methyls, has some pyramidal character, it has somewhat of a lone pair. This gives rise to a weak negative potential,  $V_{S,\min} = -5$  kcal/mole, on one side of the molecule; see Figure 5(a). On the same side, there is a weakly

positive potential over  $N_b$ , the nitro group's nitrogen, with  $V_{S,max} = +4$  kcal/mole. We were not able to find any positive maximum over the N-NO<sub>2</sub> bond, on either side of the molecule, as there is over the C-NO<sub>2</sub> in nitromethane (Figure 2). The variances,  $\sigma_z^2 = 39.8$  and  $\sigma_z^2 = 104.7$  (kcal/mole)<sup>2</sup>, are in the normal range for organic molecules.

**Table 6.** Effects of electric fields on molecular electrostatic potential of dimethylnitramine, (H<sub>3</sub>C)<sub>2</sub>N<sub>a</sub>-N<sub>b</sub>O<sub>2</sub>. Calculations at B3PW91/6-31G\*\* level

Field, $\pm x$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	102.7	58.3	39.5	39.8	39.7	58.1	98.6
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	207.5	132.7	105.3	104.7	105.7	132.2	206.9
$V_{S,min}$ , kcal/mole oxygens $N_a$	-45 -10	-40 -6	-36,-36 -5	-36,-36 -5	-36,-36 -6	-40 -7	-45 -12
$V_{S,max}$ , kcal/mole N-NO <sub>2</sub> bond $N_b$ hydrogens	--- --- 31-35	--- 5 9-29	--- 4 16-29	--- 4 17-29	--- 4 16-29	--- 5 8-29	--- --- 31-34
Field, $\pm y$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	104.5	57.8	40.7	39.8	39.5	58.1	105.0
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	103.7	102.1	104.9	104.7	102.8	101.9	102.9
$V_{S,min}$ , kcal/mole oxygens $N_a$	-38,-37 -23	-36,-36 -15	-36,-36 -7	-36,-36 -5	-36,-36 -4	-36,-36 -15	-38,-37 -23
$V_{S,max}$ , kcal/mole N-NO <sub>2</sub> bond $N_b$ hydrogens	38 --- 37	29 --- 28	--- 4 17-28	--- 4 17-29	--- 5 17-29	29 --- 28	38 --- 37
Field, $\pm z$ direction, <sup>a</sup> au <sup>b</sup>	-0.020	-0.010	-0.001	0.0	+0.001	+0.010	+0.020
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	32.3	19.0	36.9	39.8	44.1	93.3	167.9
$\sigma_z^2$ , (kcal/mole) <sup>2</sup>	19.6	46.5	97.1	104.7	110.4	160.8	238.6
$V_{S,min}$ , kcal/mole oxygens $N_a$	-15,-15 -20	-25, 25 -13	-35,-35 -6	-36,-36 -5	-37,-37 -5	-48, 48 --- <sup>c</sup>	-59 ---
$V_{S,max}$ , kcal/mol N-NO <sub>2</sub> bond $N_b$ hydrogens	28 13 4-16	23 8 15-16	--- 5 17-27	--- 4 17-29	--- 4 17-30	--- --- 44	--- --- 56

<sup>a</sup>  $N_a$  (nitrogen bearing the methyl groups) is at origin,  $N_b$  is on  $+z$  axis;  $x$ -axis is in N-NO<sub>2</sub> plane,  $y$ -axis is perpendicular to N-NO<sub>2</sub> plane.

<sup>b</sup> 1 au = 51.42 V/Å.

<sup>c</sup>  $N_a$  has changed from pyramidal to planar.

As observed for nitromethane, the  $\pm x$ ,  $\pm y$  and  $+z$  fields polarize the charge distribution of dimethylnitramine, making it more positive in one direction and more negative in the other. The effects are summarized in Table 6. The various  $V_{S,\min}$  and  $V_{S,\max}$  may be significantly shifted in position as well as changed in magnitude by the fields. For example, the 0.010 au  $+x$  field moves the  $V_{S,\min}$  of the  $N_a$  lone pair by 0.5 Å in the  $+x$  direction. The stronger fields often cause the merging of the oxygen negative regions or the hydrogen positive ones, so that a separate  $V_{S,\min}$  or  $V_{S,\max}$  for each atom can no longer be identified.

It is interesting to note that while there is no positive maximum above the N–NO<sub>2</sub> bond in ground-state (H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>, strong fields in certain directions are able to produce one. Quite high  $V_{S,\max}$  are found over this bond for  $\pm y$  and  $-z$  fields of 0.010 and 0.020 au (Table 6).

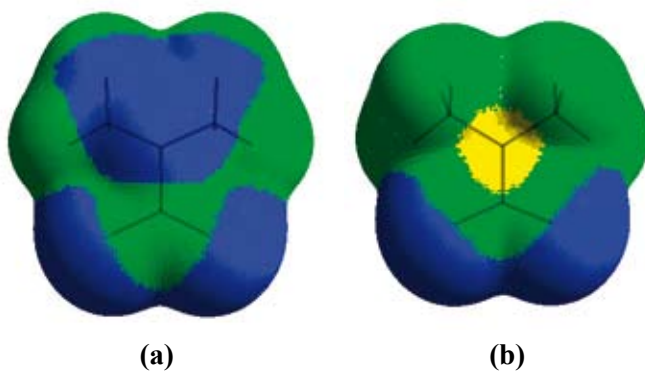


**Figure 6.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of dimethylnitramine [(H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>] in the presence of an electric field in the  $+z$  direction with a strength of 0.020 au. The hydrogens are at the top, the oxygens at the bottom. Color ranges, in kcal/mole, are: purple, more negative than  $-35$ ; blue, between  $-35$  and  $0$ ; green, between  $0$  and  $20$ ; yellow, between  $20$  and  $30$ ; red, more positive than  $30$ .

Fields parallel to the  $z$ -axis have effects similar to those described for H<sub>3</sub>C–NO<sub>2</sub>. In the  $+z$  direction, a highly polar system is obtained,  $V_S(\mathbf{r})$  again being ionic in appearance (Figure 6). The  $V_{S,\min}$  and  $V_{S,\max}$  are  $-59$  and  $+56$  kcal/mole, and  $\sigma_z^+$  and  $\sigma_z^-$  are the highest encountered in this work,  $167.9$  and  $238.6$  (kcal/mole)<sup>2</sup>, as is the dipole moment,  $-7.83$  D (Table 2). The  $+z$  fields of  $+0.010$  and  $+0.020$  au actually change  $N_a$  from pyramidal to planar, so that its lone pair and the associated  $V_{S,\min}$  are eliminated.

Fields in the  $-z$  direction lead, as for H<sub>3</sub>C–NO<sub>2</sub>, to levels of overall polarity

less than in the ground state. For a field of  $-0.020$  au, the oxygen  $V_{S,\min}$  and the hydrogen  $V_{S,\max}$  are  $-15$  and  $+4$  to  $+16$  kcal/mole, the variances are diminished, and  $\mu = -1.31$  D (Table 2). Figure 7 shows the relative weakness and low variability of this surface potential. On the other hand, the lone pair  $V_{S,\min}$  of  $N_a$  and the  $V_{S,\max}$  of  $N_b$  are larger in magnitude than for any other  $\pm z$  field, and the stronger  $-z$  fields cause positive maxima  $V_{S,\max}$  to appear above the  $N\text{--}NO_2$  bond.



**Figure 7.** Calculated B3PW91/6-31G\*\* electrostatic potential on the 0.001 electrons/bohr<sup>3</sup> molecular surface of dimethylnitramine [(H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>] in the presence of an electric field in the  $-z$  direction with a strength of 0.020 au. The hydrogens are at the top, the oxygens at the bottom. Two views are shown: (a) side of molecule with nitrogen lone pair; (b) side of molecule without lone pair. Color ranges, in kcal/mole, are: purple, more negative than  $-35$ ; blue, between  $-35$  and  $0$ ; green, between  $0$  and  $20$ ; yellow, between  $20$  and  $30$ ; red, more positive than  $30$ .

## Summary

Our purpose in undertaking this study was to assess qualitatively and to calibrate quantitatively the responses of two prototypical energetic molecules to electric fields. What are the consequences, and how sensitive are they to the strengths and directions of the fields?

For the most part, the molecular properties investigated were influenced only to rather minor extents by the  $\pm 0.001$  au fields. Bond lengths and most bond angles were relatively little affected by even the stronger electric fields. More



prevalent were conformational changes, such as rotations of methyl groups and complete or partial inversion of the pyramidal nitrogen, N<sub>a</sub>, of (H<sub>3</sub>C)<sub>2</sub>N–NO<sub>2</sub>.

The greatest changes in polarity, as reflected in the molecular surface electrostatic potentials and as measured by the dipole moments, were produced by 0.010 and 0.020 au fields along the C–NO<sub>2</sub> and N–NO<sub>2</sub> bonds; these are parallel to the largest dipole moment components of the ground-state molecules. These fields strongly reinforced or strongly counteracted the molecules' intrinsic polarities. Fields perpendicular to these axes had lesser but nevertheless sometimes quite substantial effects upon the molecular charge distributions. For both molecules, it was only the fields tending to reverse their natural polarities that increased their energies.

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