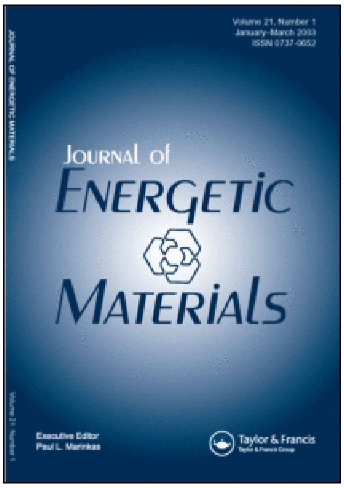

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

# Calculation of bond strengths and optimized geometries of nitroaromatics by semi-empirical methods

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**To cite this Article** Swanson, Jon T.(1987) 'Calculation of bond strengths and optimized geometries of nitroaromatics by semi-empirical methods', Journal of Energetic Materials, 5: 2, 157 — 166
**To link to this Article: DOI:** 10.1080/07370658708218546
**URL:** http://dx.doi.org/10.1080/07370658708218546

# CALCULATION OF BOND STRENGTHS AND OPTIMIZED GEOMETRIES OF NITROAROMATICS BY SEMI-EMPIRICAL METHODS

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## ABSTRACT

The size of most actual energetic materials will limit calculation of their properties to the semi-empirical methods. To calibrate the abilities of the semi-empirical methods, the geometries and bond strengths of a number of nitroaromatic compounds have been calculated by the AM1 and MNDO methods. The AM1 method does well in predicting geometries, predicting a planar $NO_2$ group in most cases. Both methods give an absolute error of about 35 kcal/mole in bond strengths. Relative effects within the group of compounds are predicted somewhat better.

## INTRODUCTION

Trinitrotoluene (TNT) is an important military and commercial explosive. As such, TNT, and the related mono- and

Journal of Energetic Materials vol. 5, 157-166 (1987)

Published in 1987 by Dowden, Brodman & Devine , Inc.

dinitrotoluenes, have been studied extensively over the past several decades. Thermal decomposition of nitroaromatics have been studied in the gas phase,[1] in the neat molten liquid,[2] and by computational techniques.[3] Studies in the gas phase indicate that C-$NO_2$ bond breaking and $NO_2$ rearrangement to the nitrite are competitive processes occuring during decomposition.[1] Bond cleavage is preferred slightly over rearrangement. Studies in the neat molten liquid are complicated by secondary reactions and the difficulty in identifying the radicals which are formed.[2c] However, hydrogen transfer followed by loss of nitrous acid or hydroxyl radical is a likely first step.

Semi-empirical molecular orbital calculations indicate that intramolecular hydrogen atom transfer has a sufficiently low activation barrier to be considered as a first step.[3b] The semi-empirical methods (MNDO[4] and AM1[5]) do tend to have large errors in calculating the heats of formation of nitro-containing compounds.[6] In comparison with values obtained from large-scale ab initio calculations and gas-phase experimental measurements MNDO predicts the bond strength of the C-$NO_2$ bond in 1-nitropropene with an error of ~35 kcal.[1,3c] However, in compounds where the environment of the $NO_2$ group undergoes little change, such as with proton transfer, agreement between semi-empirical and ab initio calculations is good, only differing by a few kcals. Because the reactions of nitroaromatics are so complex in the molten state, calculations will continue to be called upon to help elucidate the reaction mechanisms. Only semi-empirical methods are capable of calculating properties of the actual nitroaromatics themselves using a reasonable amount of computer time.

Recognizing the limitations of the semi-empirical methods in calculating absolute heats of formation for reactions involving very electron- rich systems, this paper compares geometries and relative C-$NO_2$ bond strengths for the mono-nitrotoluenes, a series of the dinitrotoluenes and 2,4,6-trinitrotoluene. The numbers obtained are compared with ab initio results and experimental results -- the crystal structure of 2,4,6-trinitrotoluene and the gas phase bond strengths recently obtained by Gonzalez, Larson, McMillan, and Golden.

## THE METHOD

The program MOPAC[7] using both the MNDO and AM1 Hamiltonians was employed on a VAX-11/780 computer. All heats of formation were calculated from the fully optimized geometry. The nitrotoluenes have a number of local minima, obtained by rotation of the nitro and methyl groups. Each local minima was evaluated to determine which was the true global minimum. In most cases the loss of $NO_2$ from the aromatic produced a sigma radical ground state. When using the AM1 Hamiltonian, SCF calculation converged on an excited state π radical, about 40 kcal above the true ground state for the radical produced by $NO_2$ loss from 2,4,6-trinitrotoluene (in either the 2 or 4 position). The ground state was found by careful selection of the starting geometry for the geometry optimization. Calculations of closed shell systems were done using the RHF formalism while the of open shell systems were evaluated using the UHF formalism.

## RESULTS AND DISCUSSION

### Geometry

Figures 1 and 2 show the optimized geometries for 2,4,6-trinitrotoluene as calculated by the MNDO and AM1 methods. Selected bond lengths and dihedrals are shown in Table I. Also shown for comparison are the results obtained by Carper, Davis, and Extine[6] from the crystal structure of TNT.[8] In general AM1 does a better job of describing the geometry of the molecule; MNDO tends to predict bond lengths which are too long and dihedral angles which are too large. The MNDO method predicts the conformation with the nitro group perpendicular to the aromatic ring to be most stable. The AM1 method predicts the planar conformation to be most stable. Unpublished ab initio calculations on 1-nitropropene done at our research labs also predict the nitro group to be most stable in the planar conformation. Some of the out of plane rotation of the nitro groups in the crystal structure of TNT is probably due to crystal packing forces. The crystal structure of nitrobenzene indicates a planar nitro group to be most stable.[9] The barrier to rotation for the nitro group in nitrobenzene is about 3.1 kcal/mole.[10] The barriers to rotation are 2.42 and 3.62

TABLE I: Bond Lengths (in Å) and Dihedrals (in degrees) for 2,4,6-Trinitrotoluene

| Nitro Ring Position | | 2 | 4 | 6 |
|---|---|---|---|---|
| MNDO | | | | |
| | C-C-N-O | 84 | 54 | 95 |
| | $C-NO_2$ | 1.510 | 1.502 | 1.510 |
| | $C-CH_3$ | 1.514 | | |
| AM1 | | | | |
| | C-C-N-O | 34 | 0 | 20 |
| | $C-NO_2$ | 1.496 | 1.491 | 1.495 |
| | $C-CH_3$ | 1.479 | | |
| CRYSTAL* | | | | |
| A | C-C-N-O | 51 | 24 | 43 |
| | $C-NO_2$ | 1.496 | 1.443 | 1.449 |
| | $C-CH_3$ | 1.505 | | |
| B | C-C-N-O | 60 | 30 | 45 |
| | $C-NO_2$ | 1.459 | 1.482 | 1.494 |
| | $C-CH_3$ | 1.507 | | |

| C-C ring | 1-2 | 2-3 | 3-4 | 4-5 | 5-6 | 6-1 |
|---|---|---|---|---|---|---|
| MNDO | 1.422 | 1.411 | 1.410 | 1.407 | 1.413 | 1.423 |
| AM1 | 1.414 | 1.403 | 1.400 | 1.400 | 1.403 | 1.416 |
| A | 1.390 | 1.364 | 1.415 | 1.375 | 1.373 | 1.408 |
| B | 1.395 | 1.383 | 1.344 | 1.373 | 1.387 | 1.379 |

*A and B refer to the two forms of TNT found in the crystal structure (see ref. 6).

kcal/mole respectively for 2-nitrotoluene and 4-nitrotoluene using AM1, favoring the planar conformation. The barriers to rotation are 5.52 and 1.69 kcal/mole, respectively for these compounds using MNDO. In the case of MNDO, the perpendicular conformation is favored.

### Energetics

The $C-NO_2$ bond strengths for the mononitrotoluenes, a series of dinitrotoluenes and 2,4,6-trinitrotoluene calculated by the MNDO and AM1 methods are presented in Table II. The gas-phase numbers of McMillan and co-workers[1] are included for comparison. All the computed bond strengths are very low. If the error in the heat of formation for nitric oxide (-22.6 kcal/mole for AM1 and -12.5 kcal/mole for MNDO) and the error in the heat of formation of nitromethane (7.8 kcal/mole for AM1 and 21.0 kcal/mole for MNDO) are used to calculate a rough correction factor one obtains corrections of 30.4 kcal/mole for AM1 and 33.5 kcal/mole for MNDO.[9] One can see from the table that correcting for the errors in the nitro groups correct most of the error in the calculation. If the correction factor can be considered constant, the relative changes in calculated bond strengths should be useful quantities.

Examining Table II shows that MNDO overestimates the effects of the ortho-methyl group and the effect of additional nitro groups. The difference between ortho and paranitrotoluene is calculated by MNDO to be 3.4 kcal/mole while experimentally the

## TABLE II: C-$NO_2$ Bond Strengths for Nitroaromatics

| | | MNDO | AM1 | Exptl Ea |
|---|---|---|---|---|
| 2-nitrotoluene | | 29.1 | 30.0 | 67.0 |
| 3-nitrotoluene | | 30.4 | 31.1 | |
| 4-nitrotoluene | | 32.5 | 31.6 | 68.2 |
| 2,4,-dinitrotoluene | 2 | 23.3 | 27.0 | 67.4 |
| | 4 | 26.9 | 28.7 | |
| 2,6-dinitrotoluene | 2,6 | 23.6 | 28.8 | |
| 2,3-dinitrotoluene | 2 | | 24.1 | |
| | 3 | | 24.9 | |
| 3,4-dinitrotoluene | 3 | | 24.6 | |
| | 4 | | 25.1 | |
| 2,4,6-trinitrotoluene | 2,6 | 18.4 | 21.9 | |
| | 4 | 23.7 | 26.3 | |

value is only 1.2 kcal/mole. AM1 does a considerably better job, predicting a 1.6 kcal/mole difference in bond energies. When a second nitro group is added, as in 2,4-dinitrotoluene both MNDO and AM1 predict a lowering of the bond dissociation energy. MNDO predicts a lowering of 5.8 kcal/mole in the ortho and 2.4 kcal/mole in the para position. The experimental results show a small increase in the bond strength. For the pair nitrobenzene and 1,3-dinitrobenzene, a slight increase is also observed, indicating the electronic effects of interacting the nitro groups are not being properly accounted for. The error may all be due to incorrectly accounting for the heat of formation difference between a nitro group in a dinitro compound and a nitro group in a mononitro radical. The calculations also predict a weakening of the C-$NO_2$ bond, presumably due to steric effects, of about 4 kcal/mole for the ortho disubstituted toluenes and a very weak ortho C-$NO_2$ bond in 2,4,6-trinitrotoluene. The TNT result may, however, be a result of incorrectly predicting the effect of the added nitro group. Experimental gas phase numbers are not available to check these predictions, however.

## CONCLUSIONS

Because of the complexity of the reactions of energetic materials, accurate calculations are required as an aid to the experimentalist. Semi-empirical calculations using the MNDO and AM1 Hamiltonians have been conducted to ascertain their ability to calculate accurate geometries and bond energies. MNDO overestimates bond lengths and both steric effects and the electronic effects of the nitro group. More importantly, MNDO incorrectly predicts the nitro group to lie perpendicular to the aromatic ring. AM1 does well in predicting molecular geometries, correctly predicting a planar $NO_2$ group, and appears to account well for steric effects, but again, does not correctly predict the electronic effect of the nitro group. Errors by both methods are about 35 kcal/mole in predicting the gas phase $C-NO_2$ bond dissociation energies. Describing the electron-rich nitro group has long been a problem for semi-empirical methods. However, ab initio programs are capable, using a reasonable amount of computer time, of calculating only the simplest molecules containing two nitro groups. Thus semi-empirical methods, and knowledge of their limitations and estimates of the errors they are likely to incur, are important to the calculation of real energetic materials of practical importance.

# REFERENCES

1. A. G. Gonzalez, W. C. Larson, D. F. McMillen, and D. M. Golden, submitted to J. Phys. Chem.

2. see for example:

   a. S. A. Shackelford, J. W. Beckmann, and J. S. Wilkes, J. Org. Chem., 42, 4201 (1977).

   b. R. M. Guidry and L. P. Davis, Thermochimica Acta, 32, 1, (1979).

   c. J. T. Swanson, L. P. Davis, R. C. Dorey, and W. R. Carper, submitted to Org. Resonance in Chem.

3. see for example:

   a. L. P. Davis and R. M. Guidry, Aust. J. Chem., 32, 1369, (1979).

   b. A. G. Turner and L. P. Davis, J. Am. Chem. Soc., 106, 5447, (1984).

   c. A. G. Turner, submitted to J. Phys. Chem.

4. M. J. S. Dewar, W. Thiel, J. Am. Chem. Soc., 99, 4899, (1977).

5. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, J. Am. Chem. Soc., 107, 3902, (1985).

6. L. P. Davis, D. M. Storch, and R. M. Guidry, submitted to J. Energetic Materials.

7. J. J. P. Stewart, Quantum Chemistry Program Exchange, No. 455, 5, No. 4, 133 (1985) (Version 3.1).

8. W. R. Carper and L. P. Davis, J. Phys. Chem., 86, 459, (1982).

9. J. Trotter, Tetrahedron, 8, 13, (1960).

10. J. H. Hog, L. Nygaard, and G. O. Sorensen, J. Mol. Structure, 7, 111, (1971).