

## TRINITROMETHYL ANION. AN AB INITIO MO STUDY OF ITS STRUCTURE

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### ABSTRACT

Several conformers of nitroform anion are studied with ab initio MO methods.

### INTRODUCTION

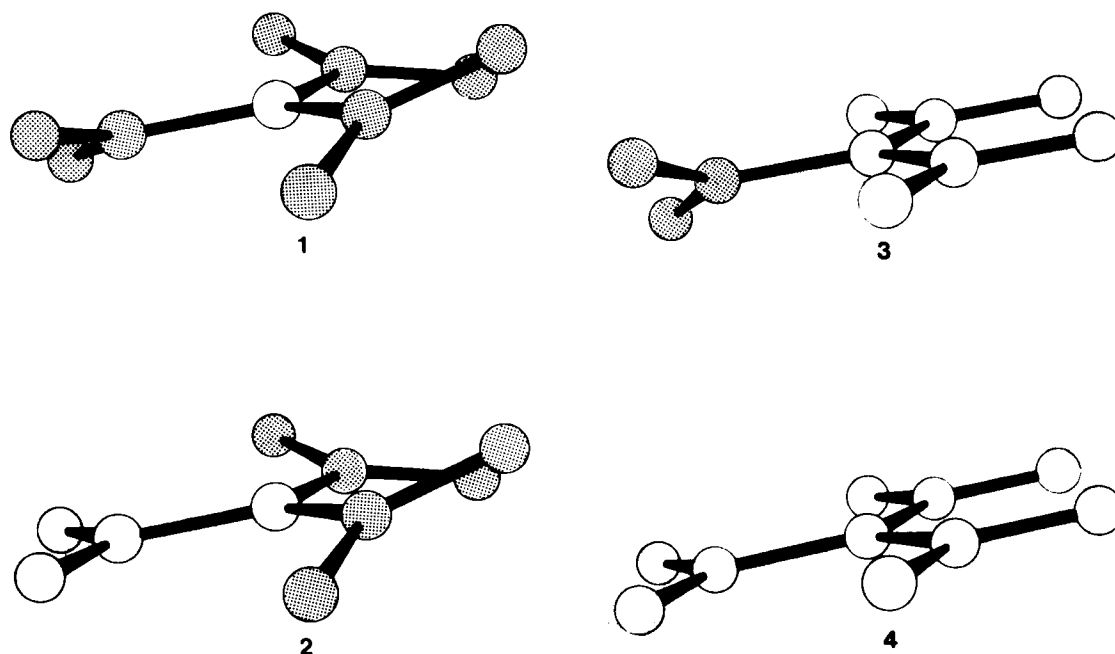
Measurements of equilibrium acidities in aqueous solutions have shown that although nitromethane is more acidic than cyanomethane by 14 pK units [1, 2], nitroform is less acidic than cyanoform by some 5 pK units [2, 3]. This discrepancy has been rationalized in terms of intrinsic as well as solvation effects [4]. In the former category, O—O repulsions between adjacent nitro groups in anions have been shown to play an important role [4], but the contrast between non-planarity of nitro groups in nitroform anion and planarity of cyano groups in cyanoform anion has often been invoked [5, 6]. The purpose of this investigation is to assess the importance of this latter factor in accounting for anomalies like the one described above.

### METHODS

Ab initio MO methods [7] were employed at two levels of approximation. Each structure was first fully optimized using the STO-3G basis set. This was followed by calculations with the STO/4-31G basis set in which bond distances were optimized but bond angles were fixed at their STO-3G optimized values. Previous theoretical studies have shown this approach to yield structures and properties which compare well with experimental quantities [8]. The following conformers of nitroform anion have been studied:  $C_3$  symmetric propeller (1),  $C_2$  species with one nitro group in the CNNN plane and the others skewed from this plane by the same angle (2),  $C_2$  species with two nitro groups in the CNNN plane and the third skewed with respect to it (3) and planar (4).\* The results are collected in Table 1.

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\*Planar nitromethyl anion is calculated to be of lower energy than pyramidal nitromethyl anion [9]. Since further substitution by nitro groups will make this energy difference larger still, we have not considered a pyramidal nitroform anion in these studies.



## RESULTS AND DISCUSSION

The STO/4-31G parameters compare reasonably well with experimental values and do not vary greatly within the conformers calculated. The most sensitive parameter is the ONO angle presumably because it reflects more directly variations in steric effects and O—O repulsions between adjacent nitro groups. Thus, the ONO angles are larger for those nitro groups which

TABLE 1

Geometries, energies and charges of conformers of nitroform anion<sup>a</sup>

	1	2		3		4
		I.P. <sup>c</sup>	O.P. <sup>d</sup>	I.P. <sup>c</sup>	O.P. <sup>d</sup>	
N—O <sup>b</sup>	1.294 (1.237)	1.294 (1.237)	1.292 (1.236)	1.296 (1.237)	1.292 (1.236)	1.297 (1.238)
C—N <sup>b</sup>	1.445 (1.398)	1.447 (1.405)	1.447 (1.424)	1.439 (1.404)	1.452 (1.425)	1.446 (1.408)
∠ONO <sup>b</sup>	121.2	120.3	120.7	120.4	120.9	119.8
Twist angle	17.1	0	17.3	0	25.1	0
Energy	0 (0)	0.4 (2.8)		0.5 (4.0)		1.3 (5.4)
Charge N <sup>e</sup>	0.137	0.111		0.098		0.112
Charge O <sup>e</sup>	-0.401	-0.390		-0.388		-0.394

<sup>a</sup>Distances in Å, angles in degrees and energies in kcal mol<sup>-1</sup>. STO/4-31G values in parentheses. <sup>b</sup>Experimental values [10]: N—O: 1.21–1.24 Å; C—N: 1.37–1.46 Å; ∠ONO: 121–124°. <sup>c</sup>Nitro groups in the C>NN plane. <sup>d</sup>Nitro groups out of the C>NN plane. <sup>e</sup>Average values.

are not in the plane of the rest of the molecule.\* The consistently larger relative energies given by the STO/4-31G method undoubtedly reflect larger steric and repulsion effects due to smaller bond distances.

<sup>14</sup>N and <sup>17</sup>O NMR spectra of solutions of trinitromethyl salts appear as a single band, even when the temperature is lowered to  $-75^{\circ}\text{C}$  [13]. This result was rationalized by the presence of a single anionic species with equivalent nitro groups.\*\* Implicit in this interpretation is the assumption that possible equilibrating species show differences in NMR chemical shifts. These latter have been found to parallel electronic charges for a series of related compounds [11, 15, 16]. The charges shown in Table 1 confirm that the assumption mentioned above is valid for the <sup>14</sup>N chemical shifts.

In the crystalline state, both the hydrazinium [10] and the potassium [17] salts of nitroform anion are present in two different forms. Each of these contains two essentially equivalent and coplanar nitro groups and one highly skewed nitro group.

The contrasting results in the crystalline state and in solution are a reflection of small conformational energy differences. These differences remain small even in the gas phase where damping by solvent is absent.

The results presented above confirm our previous conclusion that non-planarity of nitro groups in nitroform anion makes only a small contribution to the non-additivity of pK values of nitromethanes [4].

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\*For comparison, the STO-3G optimum ONO angle for trinitromethane is  $127.0^{\circ}$  [11] (Exp.:  $128.6^{\circ}$  [12]), with the closest O—O approach for adjacent nitro groups ranging from 2.4 Å for planar nitroform anion (smallest ONO angle) to 3.1 Å for trinitromethane (largest ONO angle).

\*\*Similar interpretations have been given to IR spectra of nitroform anion [14].

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