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COMPARATIVE MOLECULAR ORBITAL STUDY OF POLYNITROMETHANES AND THEIR ANIONS

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Abstract—The performance of *ab initio* STO-3G and CNDO/2 molecular orbital methods in the calculation of properties of polynitromethanes is studied.

The ready availability of computer programs for performing MO calculations has resulted in a large increase in the number of applications of them to problems in organic chemistry. Our interest in carbanion chemistry,[1,2] in particular in the acidity of polinitromethanes, has lead us to consider solvation effects by inclusion of H_2O molecules around the organic moiety. Frequently *ab initio* methods give better agreement with experimental results than semiempirical ones. However in the series to be studied only a limited number of structures are known, and geometry optimization[3] must be employed in order to assure directly comparable and unbiased results. This makes *ab initio* calculations even with the minimal STO-3G basis set[4] very expensive. Hence, before extending the studies to solvated systems, it seemed worthwhile to compare the performance of the *ab initio* method on the isolated hydrocarbons and anions with that of the less expensive CNDO/2 method.[5]

The compounds studied are nitromethane (**1**), dinitromethane (**3**), trinitromethane (**5**) and their corresponding anions (**2**, **4**, **6**).

RESULTS AND DISCUSSION

Geometries. The comparison of bond distances is presented in Fig. 1. The CNDO/2 method gives reasonable agreement with experimental data[6–10] for N–O bonds and for C–N bonds in anions, but only poor for C–N bonds in hydrocarbons. The agreement of *ab initio* results with experimental values is in general poor.

Comparison of bond angles was carried out on the ONO angle because it reflects best changes in charge distribution in the molecules studied and hence suffers substantial variations along the series. Although the results from both methods parallel each other (Fig. 2), CNDO/2 angles are consistently smaller than experimental ones, a consequence of the inability of the CNDO/2 method to properly account for non-bonded lone pair/lone pair and lone pair/π-bond interactions.[11,12]

Force constants. Force constants have been determined by calculating numerically the second derivative of the molecular energy with respect to the appropriate bond length. The results from both methods parallel each other. The absolute values lie closer to the expected values in the case of the *ab initio* method, as has been observed earlier.[13,14] Thus, experimental force constants lie in the region 4–6 mdyn/Å and 10–13 mdyn/Å for single and double bonds between first row atoms, respectively,[15] and the *ab initio* method gives average values of 5.7 and 10.4 mdyn/Å for the C–N and N–O bonds in the hydrocarbons, and 8.3 and 10.2 mdyn/Å in the anions. However, the large deviations from experimental quantities of the CNDO/2 values do not represent a serious objection to the examination of trends within a series of related compounds.[16]

Ionization potentials. These quantities also exhibit parallelism (Fig. 4) but, as expected, the absolute values are unrealistic. This is seen not only by comparison with the available experimental result,[17,18] but also in the

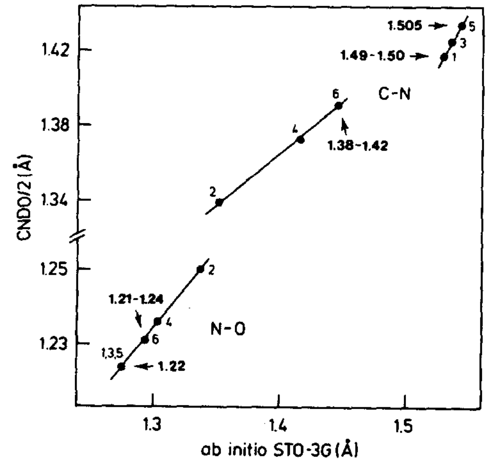

Fig. 1. Bond distances (experimental quantities in this and other figures are indicated by arrows).

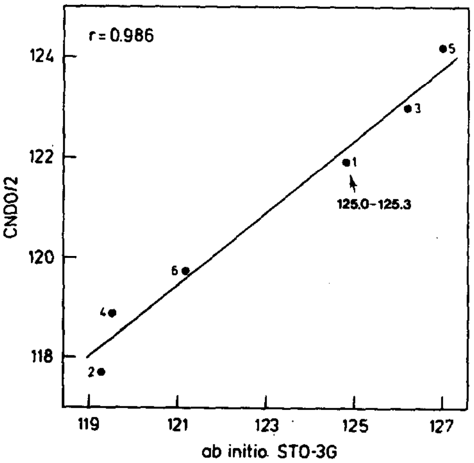

Fig. 2. ONO bond angles.

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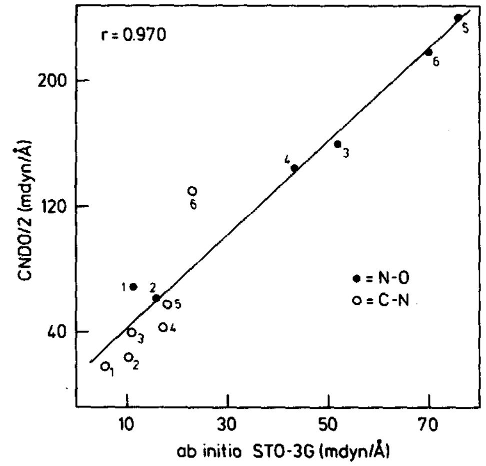

Fig. 3. Force constants.

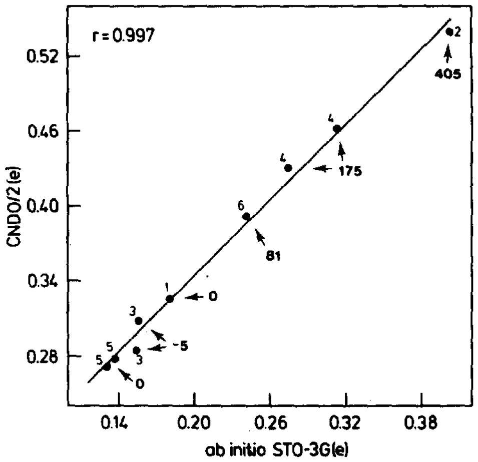

Fig. 5. Charges on oxygen.

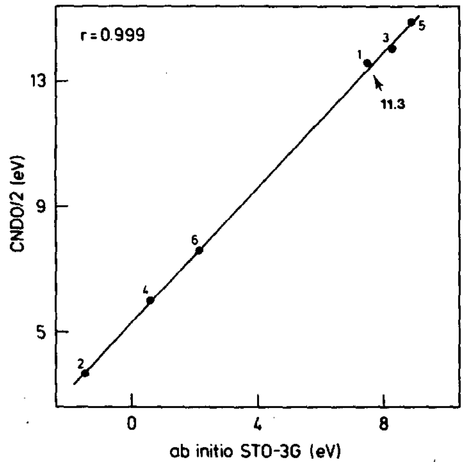

Fig. 4. Ionization potentials.

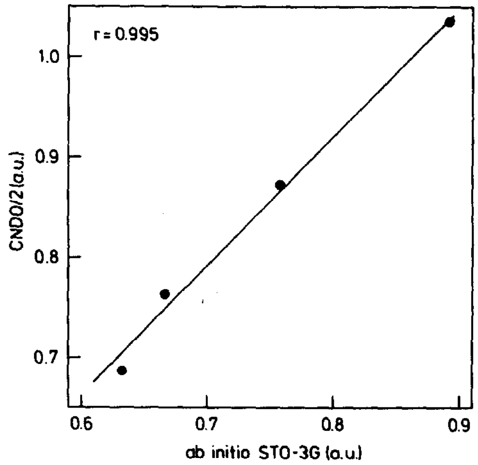

Fig. 6. Gas phase acidities.

negative ionization potential calculated by the *ab initio* method for nitromethyl anion.

The non-bonding π orbital of the nitro group in nitromethane ($^2A_2$) is calculated by both methods to be the highest occupied MO (HOMO). Although the first band of the photoelectron spectrum of nitromethane was first assigned to the σ orbitals on oxygen,[17,18] new arguments have recently been advanced suggesting this assignment to be incorrect, the $^2A_2$ orbital being the HOMO.[19]

Charges. Since oxygen atoms show the largest concentration of charge, these quantities were compared (Fig. 5). In analogy with other nuclei[20,21] an experimental indication of the charge on oxygen may be given by ^{17}O NMR chemical shifts. These quantities parallel the calculated charges (Fig. 5).

A further test is provided by dipole moments. The values calculated for compounds **1**, **3** and **5** by the CNDO/2 method (4.25, 4.28 and 3.67 D) and the *ab initio* methods (3.18, 3.22 and 2.41 D) also parallel each other. The experimental value for **1**, 3.46 D,[23] lies closer to the *ab initio* result.

Gas phase acidities. The energy differences between anions and hydrocarbons calculated with both methods parallel each other (Fig. 6). A comparison with experimental data is the subject of the accompanying paper.[24]

CONCLUSIONS

Within the series of nitromethanes trends in various parameters calculated with the CNDO/2 and *ab initio* STO-3G MO methods closely parallel each other as well as experimental trends. Agreement with experimental quantities in absolute terms favours *ab initio* in some instances and CNDO/2 in others.

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