Theoretical Calculations of Chemical Interactions. Part 5.[1] 1,1-Disubstituted 2,4,6-Trinitrocyclohexadienylide ('Meisenheimer') Complexes

N. Sbarbati Nudelman* and Patricio MacCormack
Departamento Química Orgánica, Facultad de Ciencias Exactas, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, Piso 3, 1428 Buenos Aires, Argentina

All-valence-electron MNDO SCF-MO calculations with almost complete geometry optimization have been performed on 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide. The computed geometrical parameters have been compared with *X*-ray data. Charge distributions have been calculated for this complex and for 2,4,6-trinitroanisole, and the differences in electron densities for each atom compared with the ^{1}H and ^{13}C n.m.r. chemical shifts for both compounds. Similar calculations have been performed for 1,1-difluoro-2,4,6-trinitrocyclohexadienylide and for picryl fluoride. The results have been compared with available ^{1}H n.m.r. data. The reasonable good agreement between calculated and experimental data indicates that for these systems the MNDO method can be safely used to calculate properties of species not yet amenable to experiment.

Properties of intermediates and transition states play an important role in discussions of chemical reactivity. Considerable efforts are being devoted nowadays to the evaluation and prediction of the properties of such structures by theoretical methods.[2–5] Complexes of the 'Jackson–Meisenheimer' or 'Meisenheimer' type[6] are intermediates in the firmly established two-step mechanism of nucleophilic aromatic substitutions,[7] and knowledge of their electronic and energetic properties could contribute to a better understanding of the factors influencing mechanism(s) and reactivity in this process.

Considerable progress has been made in recent years in the structural[8] and kinetic[9] characterization of these complexes, and comparison of experimental data with the theoretical calculations may provide a reliable measure of the validity and extent of the theoretical predictions.

Results and Discussion

Method of Calculation.—Although *a priori* there might be criticism of semiempirical MO methods for calculations on ions, since the parameters in such theories were designed for neutral molecules, Dewar's MINDO/3 and MNDO methods have been successfully applied recently to calculations on ions.[10,11] Geometry optimization is inevitable in ions; therefore the MNDO program[12] in conjunction with the Davidon–Fletcher–Powell procedure[13] was adopted here. The standard program was modified to an extended basis of maximum 99 atomic orbitals. Almost complete geometry optimization was performed in all cases, except that the methyl group variables were assumed to be identical with those of the methoxide anion. Optimization was performed by use of the DFP algorithm with the 'direct' program parameters. The computation was carried out with an IBM 370 computer at IBM Argentina.

Table 1. Geometrical parameters for 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (**1**)

Bond[a]	Calc.	Exp.[c]	Bond[a]	Calc.	Exp.[c]
C(1)–C(2)	1.553	1.516	N(2)–O(5)	1.218	1.256
C(2)–C(3)	1.384	1.356	N(2)–O(6)	1.218	1.237
C(3)–C(4)	1.428	1.391	N(3)–O(7)	1.212	1.243
C(4)–C(5)	1.428	1.397	N(3)–O(8)	1.221	1.207
C(5)–C(6)	1.384	1.353	Distance[a]		
C(6)–C(1)	1.553	1.475	C(2)–C(8)	3.08	2.95
C(1)–O(1)	1.410	1.429	C(6)–C(8)	3.08	2.95
C(1)–O(2)	1.411	1.422	Angle[b]		
O(1)–C(7)	1.406	1.438	O(1)–C(1)–O(2)	101	100
O(2)–C(8)	1.406	1.448	C(2)–C(1)–C(6)	110	109
C(2)–N(1)	1.485	1.439	O(3)–N(1)–O(4)	118	123
C(4)–N(2)	1.428	1.387	O(5)–N(2)–O(6)	119	121
C(6)–N(3)	1.484	1.456	O(7)–N(3)–O(8)	117	121
N(1)–O(3)	1.212	1.220	C(7)–O(1)–C(1)	124	115
N(1)–O(4)	1.221	1.237	C(8)–O(2)–C(1)	124	115

[a] In Å. [b] In degrees. [c] Ref. 14; errors in bond lengths: ±0.017 [C(1)–C(2) to C(6)–C(1)]; ±0.019 [C(1)–O(1) to N(3)–O(8)].

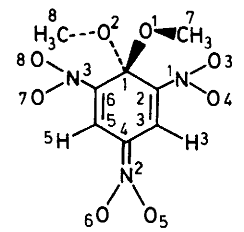

Figure 1. 1,1-Dimethoxy-2,4,6-trinitrocyclohexadienylide (**1**)

1,1-*Dimethoxy*-2,4,6-*trinitrocyclohexadienylide* (**1**).—*Geometrical parameters.* Table 1 shows the geometrical parameters (bond lengths and angles) calculated by the MNDO method and those obtained by *X*-ray diffraction in the solid state.[14] Comparison indicates satisfactory agreement between calculated and experimental values. In fact, in spite of the fact that the first set corresponds to parameters *in vacuo* whereas the second applies to the crystals, the differences are within the error of the method for stable compounds.[15] The calculated C–C bonds are only 2—3% longer than the experimental lengths, confirming the structure shown in Figure 1.

The most important difference between the two sets of data is that MNDO predicts a symmetric complex whereas the *X*-ray structure is slightly non-symmetric. The asymmetry in the crystals is due to the location of the counterions (potassium in this case). It is reasonable to assume that this asymmetry no longer holds in the gas phase, or even in solution; we will return to this point when discussing n.m.r. data.

The counterion affects not only the C(1)–C(2) and C(1)–C(6) distances, but also the nitro-group co-ordinates. The differences in the N(2)–O(5) and N(3)–O(7) bond lengths in the crystal are greater than the error; O(5) and O(7) are the oxygen atoms nearest to the potassium ion. In good agreement with the experimental data and current electronic theories, MNDO

Table 2. Calculated charge densities[a]

Atom	2,4,6-Trinitroanisole (TNA)	Complex (**1**)
C(1)	0.33	0.49
C(2); C(6)	−0.16	−0.32
C(3); C(5)	0.14	0.19
C(4)	−0.14	−0.34
H(3); H(5)	0.14	0.10
C(7); C(8)	0.25	0.24
H (average/methyl)	0.013	−0.013

[a] In electrons.

Table 3. ^1H N.m.r. chemical shifts[a]

Atom	Solvent	TNA	Complex (**1**)
H(3)[H(5)]	Me_2CO[b]	9.07	8.9
H(3)[H(5)]	Me_2SO[c]	9.07	8.64
H(3)[H(5)]	MeCN[c]	8.92	8.78
H(Me)	Me_2SO[c]	4.07	3.03

[a] δ Values. [b] R. Foster and C. A. Fyfe, *Tetrahedron*, 1965, **21**, 3363. [c] M. R. Crampton and V. Gold, *J. Chem. Soc.*, 1964, 4293.

Table 4. ^{13}C N.m.r. chemical shifts[a]

Atom	TNA[b]	Complex (**1**)	$\Delta\delta_{n.m.r.}$	$\Delta\delta_e$
C(1)	153.1	104.3	−48.8	0.16
C(2); C(6)	145.6	129.2	−16.4	−0.16
C(3); C(5)	125.3	131.2	5.9	0.05
C(4)	142.5	119.3	−23.3	−0.20
C(7); C(8)	66.4	53.2	−13.2	−0.01

[a] δ Values. [b] Ref. 17*a*.

predicts a strong double-bond character for the C(4)–N(2) bond, stronger than that of the bonds with the *ortho*-nitro groups. A slightly greater difference (~0.025 Å) than experimental error is observed for the bonds of the oxygen atoms with C(1) and the methyl carbon atoms. MNDO correctly predicts sp^3 characters for these bonds. The rest of the bond lengths can be considered satisfactorily reproduced within experimental error.

The MNDO method takes into account directional effects in bond formation; this is evident from the good agreement between calculated and experimental bond angles shown in Table 1. The large calculated angle (124°) is also in accordance with recent considerations related to the difference in reactivity between this type of complex and spiro Meisenheimer complexes.[16]

N.m.r. data. The MNDO-predicted charge densities show satisfactory agreement with ^1H and ^{13}C chemical shifts. Table 2 lists calculated charge densities for 2,4,6-trinitroanisole (TNA) and the Meisenheimer complex (**1**). Tables 3 and 4 show reported ^1H and ^{13}C chemical shifts for both compounds.

Protons H(3) and H(5) support the same charge density according to Table 2, which predicts the identical n.m.r. chemical shifts observed for these protons in various solvents (Table 3). This proton equivalence shows the symmetry of the complex in solution as already discussed. In accord with this symmetry, the methyl protons are also equivalent (Table 3), in agreement with the structure (**1**) (Figure 1) and the corresponding calculated geometrical parameters of Table 1. Finally, comparison of the hydrogen charge densities of TNA and the complex (**1**) (Table 2) shows a charge shift towards the hydrogen atoms on going from TNA to the complex, in perfect agreement with the observed increased shielding of those atoms (Table 3).

Table 4 shows the ^{13}C n.m.r. chemical shifts for TNA and (**1**), and the differences in chemical shifts ($\Delta\delta_{n.m.r.}$) and the charge densities ($\Delta\delta_e$). An excellent correlation is observed for those carbon atoms that retain their sp^2 configuration; the value (close to 120 p.p.m. per electron) compares well with that obtained by Olah for the benzene–cyclohexadienyl pair (150 p.p.m. per electron).[17] A greater difference is obtained for C(1); this is reasonable since it changes from sp^2 to sp^3 configuration. The observed value of $\Delta\delta_{n.m.r.}$ is not in agreement with the predicted charge-density difference, which follows the known charge alternation.

Table 5. Geometrical parameters for picryl fluoride (PF) and 1,1-difluoro-2,4,6-trinitrocyclohexadienylide (**2**)

Bond[a]	PF	(**2**)	Angle[b]	PF	(**2**)
C(1)–C(2)	1.427	1.555	F(1)–C(1)–F(2)		105.3
C(1)–F(1)	1.313	1.362	O(1)–N(1)–O(2)	123.2	119
C(4)–N(2)	1.507	1.470	O(3)–N(2)–O(4)	122.8	119
N(1)–O(1)	1.207	1.218	O(5)–N(3)–O(6)	123.2	119
N(1)–O(2)	1.207	1.213	C(2)–C(1)–C(6)	117.9	110.4
N(3)–O(6)	1.208	1.218			

[a] In Å. [b] In degrees.

Table 6. Calculated charge densities[a]

Atom	PF	(**2**)
C(1)	0.31	0.57
C(2)	−0.12	−0.32
C(3)	0.11	0.21
C(4)	−0.09	−0.33
F	−0.12	−0.23
H(3), H(5)	0.12	0.10
N(1)	0.49	0.52
O(1)	−0.29	−0.40
O(2)	−0.29	−0.35
N(2)	0.48	0.52
O(3)	−0.30	−0.40
O(4)	−0.30	−0.40

[a] In electrons.

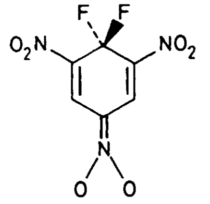

Figure 2. 1,1-Difluoro-2,4,6-trinitrocyclohexadienylide (**2**)

Heats of formation. MNDO has been parametrized to reproduce experimental heats of formation of neutral molecules; it would not be expected *a priori* to give good values for ions. In addition, it is well known that in reactions that involve ionic species solvation plays a dominant role. Nevertheless, although not good for absolute values, the method reproduces the exothermic character of the complex formation. In fact, the difference between the heats of formation of (**1**) and the reactants is −84 kcal mol^{-1}. This value is rather high in comparison, for example, with the −20.5 kcal mol^{-1} enthalpy of reaction for the formation of (**1**) in Me_2SO–MeOH (95.4:4.6),[18] but it has the correct sign and order of magnitude. Experimental studies of the reactants and the complexes have been carried out in a wide range of MeOH–Me_2SO mixtures,[18,19] and it has been observed that solvent polarity greatly influences not only complex stability but also the methoxide ion heat of transfer (ΔH_T), in opposite directions. For the small, 'hard' (in HSAB theory[20,21]) methoxide ion, ΔH_T increases with increasing content of Me_2SO in the MeOH–Me_2SO mixtures, whereas the opposite is observed for the large polarizable anion (**1**).

Furthermore, the effects of the counterion have not been taken into account in the calculations since MNDO does not include metal atoms in its parameter set. Therefore the agreement in sign and order of magnitude between the calculated *in vacuo* and the experimental solution heats of reaction can be considered reasonably good for a method not originally conceived for calculations on ions[22] and which did not include nitroaryl compounds in the original parametrization reference set.[23]

1,1-*Difluoro*-2,4,6-*trinitrocyclohexadienylide* (**2**).—Of special interest in predicting chemical reactivity and reaction mechanism(s) in nucleophilic aromatic substitution are the complexes formed in the reactions of halogenonitrobenzenes. We have performed calculations on the only complex of this type for which n.m.r. data are available: the complex formed in the reaction of picryl fluoride (PF) with potassium fluoride in crown ethers[24] (Figure 2).

Table 5 lists some calculated geometrical parameters for PF and the complex (**2**). (Only those geometrical parameters that differ by > ±0.005 Å or ±0.5° from the data recorded in Table 1 are given.)

The complex (**2**) shows a symmetric charge distribution (Table 6); the ring supports a greater negative charge than in the complex (**1**). In comparing the calculated charge density of H(3) with n.m.r. data it can be seen that MNDO predicts not only the equivalence of H(3) and H(5) but also the observed paramagnetic shift (δ 8.7 for the complex and 9.1 for picryl fluoride).[24] The data of Tables 5 and 6 are especially useful since *X*-ray data for the complex (**2**) are not available.

Conclusions

MNDO calculations with almost complete geometry optimization have been applied to a classical Meisenheimer complex (**1**) and to a halogenonitroaryl complex (**2**) of the type usually found in nucleophilic aromatic substitution. The agreement between calculated and experimental (n.m.r. and *X*-ray when available) data is remarkably good. The present and the previously reported results show the usefulness of theoretical predictions of geometrical, electronic, and energetic properties of organic molecules and ionic complexes when such data are not yet amenable to experiment. Calculations on the complexes formed with amines are in progress.

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