

CONFORMATIONS AND CHARGE DISTRIBUTIONS IN 1,2-DINITROSOETHYLENE AND FUROXAN: 2.-AB INITIO ELECTROSTATIC POTENTIALS AND RELATIVE BOND STRENGTHS

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Abstract: The bond orders and the electrostatic potentials for 1,2-dinitrosoethylene and furoxan have been calculated by means of an ab initio SCF-MO procedure (GAUSSIAN82). Calculations demonstrate that in both the trans and the cis 1,2-dinitrosoethylene the presence of the two nitroso groups weakens the C=C bond relative to ethylene. Also their di-N-oxide like structures have been found to have a substantial resonance contribution. Calculated electrostatic potentials support this view and show that the introduction of NO completely eliminates the negative region associated with the carbon-carbon double bond, thus rendering the nitroso oxygen as the preferred site for initial electrophilic interaction. In the furoxan molecule a larger bond energy has been calculated for the C₄-N₅ bond than for the C₃-N₂ bond because there is no likely resonance contributor to furoxan in which there is a simple bond between C₄ and N₅. The electrostatic potential analyses reveal that the extraannular oxygen and the N₅ are the preferred sites for initial electrophilic interaction.

Introduction

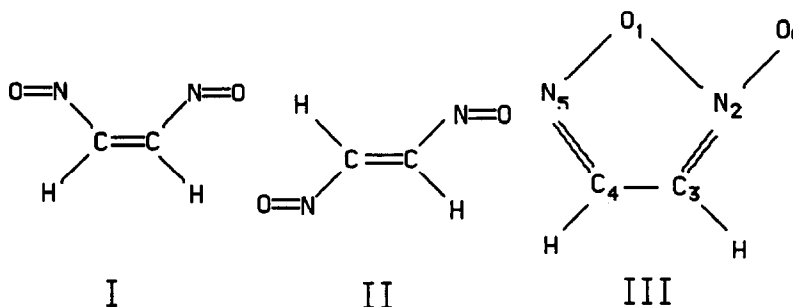
In a recent paper ¹ we have studied the structural and electronic properties of 1,2-dinitrosoethylene and furoxan using ab initio molecular orbital procedures. We have found that it is absolutely necessary to optimize the molecular geometry with basis sets including d-type functions, in order to obtain reliable structures. Calculations at the 4-31G* level demonstrate that the electronic structures of both the *cis*- and the *trans*- 1,2-dinitrosoethylene isomers are mainly determined by the cooperative enhanced charge withdrawal of the two nitroso groups. The overall result is a strengthening of the two C-N bonds and a weakening of the C=C bond (relative to nitrosoethylene). In the furoxan (or furazan N-oxide) molecule a noticeable charge withdrawal of electronic charge by the extraannular oxygen from the furazan ring was reported. Also the exocyclic N-O bond has been described as σ donation - π acceptance by nitrogen.

Along with these electronic and structural properties it is important to understand and give sound guides to the reactive behaviour of these molecules, which have stirred up considerable experimental interest ², both as transient species in ring isomerization reactions and for synthetic purposes in the

nucleophilic opening of annelated furoxans to dinitroso compounds.. With these objectives in mind we have focused upon bond strengths, as predicted by Politzer's bond energy - bond order relationship³ and molecular electrostatic potentials^{4,5}. The latter represents an attempt to extract from the properties of the isolated molecule some useful information about its behaviour as it interacts with other molecules and is well established as a guide to the reactive behaviour of molecules.

Results and Discussion.

The optimized 4-31G* structures¹ of both the *cis* (I) and the *trans* (II) isomers of 1,2-dinitrosoethylene and the furoxan (III) were used in calculating the bond orders and the electrostatic potentials.



For the former, 4-31G* basis sets were used to calculate the force constants k (in $\text{mdyn}/\text{\AA}$) and then the bond orders were calculated as

$$\text{Bond order} = 0.55747(k/R_e)^{1/2} \quad (1)$$

where R_e is the 4-31G* equilibrium bond length (in \AA). Politzer et al. have shown³ that experimentally measured bond dissociation energies correlate well with bond orders calculated using equation 1. Hence it represents a practical means for predicting the relative strengths of chemical bonds, particularly when it is a given type of bond in different environments. The electrostatic potential $V(r)$ was computed with STO-5G basis sets as

$$V(r) = \sum_A Z_A \cdot |r - R_A|^{-1} - \text{tr}(\mathbf{P} \cdot \mathbf{V}) \quad (2)$$

where Z_A is the charge on nucleus A, located at R_A , \mathbf{P} is the total density matrix and $V_{\mu\nu} = \langle \mu | |r - r|^{-1} | \nu \rangle$ is the matrix element of the coulombic potential operator $|r - r|^{-1}$ and $\{\phi_\mu | \mu=1,2,\dots\}$ is the basis functions set. The electrostatic potential is a real physical property, which can be determined experimentally as well as computationally, and is related to the electronic charge distribution. Therefore it can be used to study the approaching channels of molecules, because at this stage the interactions are

weak so that the frozen charge distribution approximation is valid. Even electrostatic calculations are in substantial agreement with SCF calculations performed by keeping the internal coordinates of the partners unaltered. Such second approximation allows for mutual polarization effects, the non-classical exchange contributions to the energy, and to some extent the charge transfer effects. The accord between the two approximations is of course better at larger distances, but it is also present at intermediate values of the approach coordinate⁶; in such a way that the electrostatic potential has proven to be an effective means for interpreting and predicting the initial reactive sites of molecules^{4,5}.

Bond orders .1. 1,2-dinitrosoethylene.- Table I shows the bond orders calculated according to equation 1, which will be taken as measures of the relative strengths of chemical bonds of a given type. Thus, inspection of these data reveals that

TABLE I

Molecule	bond	bond order	4-31G* optimized bond lengths (Å) ^a
<i>trans</i> 1,2-dinitrosoethylene	C-C	1.648	1.433
	C-N	1.942	1.262
	N-O	2.034	1.206
	C-H	1.454	1.090
<i>cis</i> 1,2-dinitrosoethylene	C-C	1.405	1.502
	C-N	1.980	1.279
	N-O	2.216	1.190
	C-H	1.528	1.069
	N-N	0.924	1.666
Furoxan	C ₃ -C ₄	1.851	1.407
	C ₄ -N ₅	2.397	1.273
	N ₅ -O ₇	1.574	1.383
	O ₁ -N ₂	1.583	1.377
	N ₂ -C ₃	1.908	1.301
	N ₂ -O ₆	2.112	1.203
	C ₃ -H ₈	1.573	1.060
	C ₄ -H ₇	1.574	1.063

^aTaken from reference 1.

the C-C bond is weaker in the *cis* 1,2-dinitrosoethylene relative to its *trans* isomer. This effect corroborates the stronger effective inductive charge withdrawal of the NO groups from the C-C bond in the *cis* conformation with respect to the *trans* conformation, which we found on the basis of bond lengths and electron density population analysis¹. The C-H bond orders appear to be larger for the *cis* isomer than for the *trans* isomer due to the strengthening effect that strong inductive withdrawers of electronic charge have on adjacent C-H bonds⁷.

Another interesting feature that is brought out by Table I is that the calculated C-N bond orders

The C-H bonds have been calculated to have larger bond orders in furoxan than in 1,2-dinitrosoethylene. Their bond orders of 1.57 are to be compared with the C-H bond order value of 1.60 found in nitrosoacetylene and in nitroacetylene⁷.

A final feature of Table I is that the extraannular N-O bond energy is smaller than the nitroso N-O bond order of the *trans* 1,2-dinitrosoethylene and larger than the nitroso N-O bond energy of the *cis* 1,2-dinitrosoethylene. The exactly reverse correlation has been found for the 4-31G* optimized bond lengths.

Electrostatic Potentials . 1. 1,2-dinitrosoethylene. The electron withdrawing power of the nitroso group can be placed in perspective by examining the calculated electrostatic potential in the molecular plane of both the *cis* and the *trans* 1,2-dinitrosoethylene (Figures 2 and 4) and comparing them to the corresponding potential for ethylene⁹. The large negative region associated with the double bond in ethylene is completely eliminated by substitution of the nitroso groups. The end result is a buildup of positive electrostatic potential above the C-C bond. For the *trans* isomer (figure 4), this buildup of positive potential separates the two large negative potential regions at both ends of the molecule, which are associated with the NO groups.

Conversely, for the *cis* isomer a nodal surface separating the positive potential end of the molecule associated with the carbon-carbon bond and the negative potential end associated with the NO groups is observed (Figure 2).

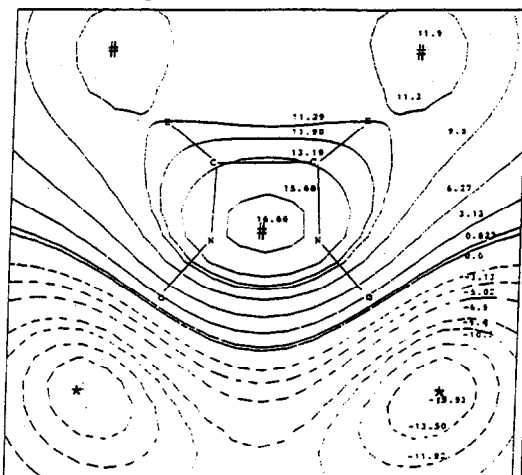


Fig.1.: Calculated electrostatic potential of the *cis* 1,2-dinitrosoethylene 1.75 Å above the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by * and # respectively.

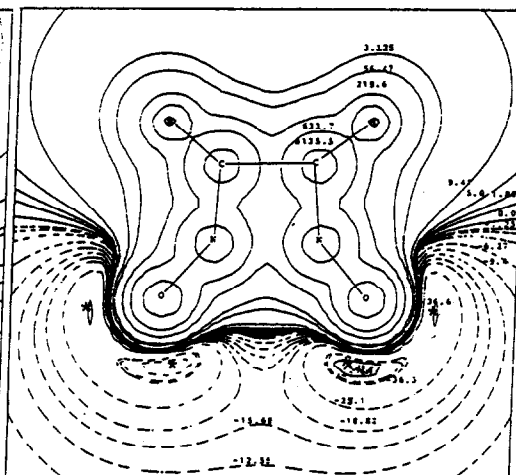


Fig.2.: Calculated electrostatic potential of the *cis* 1,2-dinitrosoethylene in the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by *.

The major negative regions of the *trans* 1,2-dinitrosoethylene are associated with the nitrogen (-35.9 kcal/mol) and oxygen (-26.1 kcal/mol) atoms (Figure 4) and can be regarded as reflecting their lone pairs. The relatively strong nitrogen and oxygen negative potentials in the *trans* 1,2-dinitrosoethylene can be put into perspective by comparing them to the nitrogen (-46.7 kcal/mol)

and oxygen (-28.5 kcal/mol) lone pair electrostatic potentials in the dinitrosoacetylene⁷. By inspection of Figure 2 we observe that the electrostatic potential minimum associated with the nitrogen lone pair does not occur in the *cis* 1,2-dinitrosoethylene and that the oxygen lone pair electrostatic potential minimum is stronger (-42.4 kcal/mol) with respect to its value for the *trans* isomer (-26.1 kcal/mol).

Unlike the nitrosobenzene¹⁰, nitrosoacetylene and dinitrosoacetylene⁷, the 1,2-dinitrosoethylene does not present positive potential buildups above the C-N-O angles (see Figures 1 and 3), but positive

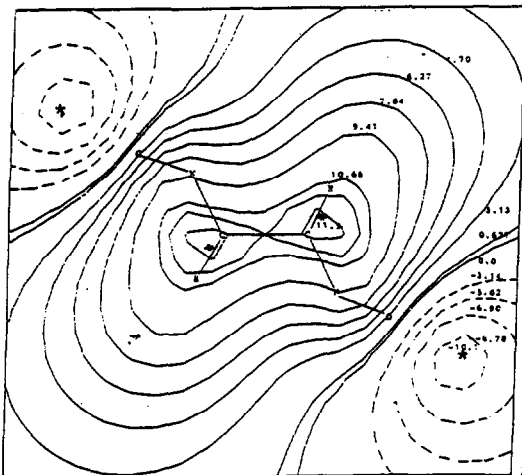


Fig.3.: Calculated electrostatic potential of the *trans* 1,2-dinitrosoethylene 1.75 Å above the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by * and # respectively.

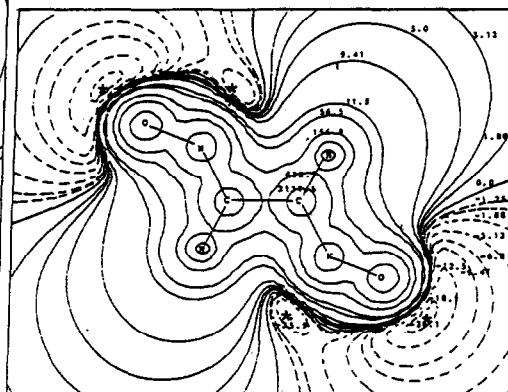


Fig.4.: Calculated electrostatic potential of the *trans* 1,2-dinitrosoethylene in the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by *.

buildups like those found for the nitrosoacetylenes⁷ above the C-H bond do occur for the *trans* 1,2-dinitrosoethylene (Figure 3). However it is worth mentioning a positive potential buildup has been found just above the N-C-C-N moiety for the *cis* 1,2-dinitrosoethylene (see figure 1).

2. Furoxan. Electrostatic potential energy maps for furoxan are reported in Figures 5 and 6. Figure 6 refers to the molecular plane and Figure 5 to a plane 1.75 Å above it. We observe that the molecular space is partitioned by a nodal surface into two different portions, one with positive potential where the approach of electrophiles is disfavored and the other one with negative potential where the initial interaction with electrophiles is favored. Since $V(r)$ represents the interaction energy at the first order perturbation theory of the molecule with a unitary point charge, an approaching electrophile's initial tendency is to go to those points at which the most negative values of the potential occur. To the extent that electrophilic attack on furoxan does occur, Figure 5 suggests that the extraannular oxygen should be the preferred site for the initial interaction. Its interaction energy at the minimum is -13.56 kcal/mol. Another possible favored reactive site toward electrophiles should be the N₅ position, where we have found a minimum interaction energy of -10.96 kcal/mol.

The positive potential region of the molecular space appears to be associated with the H-C-C-H moiety, however it is worth noting that a positive potential buildup occurs above the C₃-N₂ bond. Similar positive regions have been reported associated with the C-N bond for a number of nitrosoaromatics^{11,12}, nitrosoacetylene⁷, and nitrosobenzene¹⁰, and they have been related to the tendencies of these molecules to undergo nucleophilic attack upon the C-N bonds⁷.

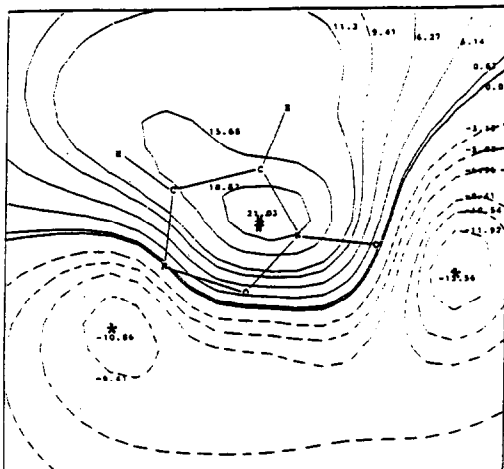


Fig.5: Calculated electrostatic potential of furoxan 1.75 Å above the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by * and # respectively.

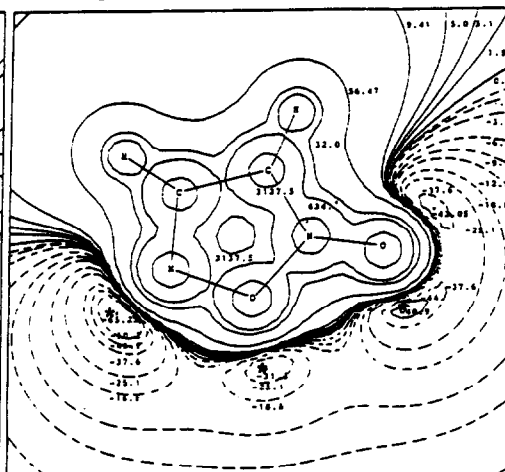


Fig.6: Calculated electrostatic potential of furoxan in the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potential; all values are in kcal/mol. The location of the planar minima and maxima are shown by *.

Figure 6 shows the electrostatic potential map for the ring plane of furoxan. We see that the major negative regions are associated with the nitrogen and oxygen atoms, and can be regarded as reflecting their lone pairs. The potential hole is deeper for N₅ than for the oxygen atoms, which is a general pattern followed by most five-membered rings containing the N and O heteroatoms^{5,14}. The relatively strong N₅ negative potential, reaching a minimum of -65.23 kcal/mol, confirms our expectation that this is a possible reactive site for electrophiles¹³.

Summary.

We have computed the bond orders and the electrostatic potential for 1,2-dinitrosoethylene and furoxan with the objective of gaining insight into the nature of the intramolecular interactions of the nitroso group with the carbon-carbon double bond and the primary extramolecular interactions with other molecules. We have seen that the presence of the two nitroso groups weakens the C=C bond relative to ethylene in both the *trans* and the *cis* 1,2-dinitrosoethylene. It is also of interest to note that a substantial contribution of the di-N-oxide like structures IV and V of the *trans* and the *cis* 1,2-dinitrosoethylene respectively comes out from the analysis of the C-N and N-O bond orders of 1,2-dinitrosoethylene. In the furoxan a larger bond energy has been found for the C₄-N₅ bond than for the C₃-N₂ bond because there is no likely contributor to furoxan in which there is a simple bond between C₄ and N₅. This effect emphasizes the reduced probability of the furazan ring to delocalize its excess of charge by resonance. The C-H bonds appear to be stronger in both 1,2-dinitrosoethylene and

furoxan than in ethylene. This would be fully consistent with the strengthening effect that strong inductive withdrawers of electronic charge have on adjacent C-H bonds.

Examining the electrostatic potential maps we have observed that the strong negative potential associated with the double bond of ethylene is entirely eliminated by the substitution of the nitroso groups. Also we have seen that the deep electrostatic potential associated with the nitroso nitrogen lone pair does not occur for the *cis* 1,2-dinitrosoethylene. This suggests that the *cis* 1,2-dinitrosoethylene can as well be formally described as the di-N-oxide of the four membered 1,2-diazetidene ring (structure V). This produces the strongest negative electrostatic potential that is associated with the oxygen atom and should be regarded as a very reactive site toward electrophiles. In the furoxan molecule two favored sites for initial electrostatic interaction have been found, i.e. : the extraannular oxygen and the N₅ atom.

Their relative affinity toward electrophiles has been put into perspective by comparison of the potential minima associated with each site.

Finally positive potential buildups that are found above the N-C-C-N moiety in the *cis* 1,2-dinitrosoethylene, above the C-H bonds regions in the *trans* 1,2-dinitrosoethylene and above the C₃-N₂ bond are other interesting features of these molecules.

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