O_0 and the carboxamide group on C^α. The peptide dihedral angle ω_0 is twisted slightly out of plane, which agrees with the X-ray results of Karle.[11] Structure **3b** ($\omega_0 = 7.6°$) exhibits less twist than **3a** ($\omega_0 = 12°$), which suggests that the twisting is partially due to 1:3 hydrogen bond formation. the ϕ_1 and ψ_1 angles are in good agreement with the respective experimental results and with the results of Cabrol et al.[4] The angle ϕ_1 is related to the $C_0N_1C_1{}^\alpha C_1{}^\beta$ angle which describes the puckering of the ring. As such, it might be expected to differ from the experimental values. However, this difference is very small, as seen in Table II.

Table III shows that **3a** is the most stable conformation for *N*-acetylproline amide. Since the calculations did not take into account solvent effects and can not reproduce the solid-state environment, the calculated results should more closely resemble experimental results in the gas phase or a nonpolar solvent. Indeed, they best reproduce the results obtained for *N*-acetylproline methylamide in carbon tetrachloride.[13] In this solution the intramolecular 1:3 hydrogen bond is present, while in the crystalline state[14] intermolecular hydrogen bonding is observed. Since in the gas-phase intermolecular hydrogen bonding is not considered, structure **3b** is higher in energy than **3a** by 3.7 kcal/mol. This energy difference is an estimation of the strength of the 1:3 hydrogen bond and is typical of a strained hydrogen bond. This bond is strained because the $O_0H_2N_2$ angle is 149° instead of the more favorable 180°. This angle and the 1.80-Å distance between O_0 and H_2 agree well with the values of 138° and 1.78 Å predicted for the 1:3 hydrogen bond of the γ turn.[5] The estimated hydrogen bond energy of 3.7 kcal/mol is close to the value of 4.5 kcal/mol found by Nemethy and Printz[5] (a molecular mechanics calculation). Their ψ_1 and ω_0 angles are also in good agreement with our results and in good agreement with the experimental data of ref 11.

As shown by Bandekar and Krimm,[20] for $CH_3CO(\text{L-Ala})_3NHCH_3$, in a γ turn the $H_i + 2 - O_i$ distance is in the range 1.86–2.13 Å, close to the 1.8-Å value found in this work. Their ϕ_2 and ψ_2 angles, called in this work ϕ_1 and ψ_1 agree with our result for the structures they call γ_m and γ_l, where γ_m contains an equatorial C_7.

Structure **3c** is much higher in energy than **3a** because of the repulsion between the negatively charged oxygens O_0 and O_2. This structure does not represent a local minimum but only a point on the energy surface.

The cis structure **3d** is higher in energy than **3a** by 4.1 kcal/mol. This energy difference, which is due to the loss of the hydrogen bond, is very close to the value of 3.7 kcal/mol between **3a** and **3b**. Replacing the acetyl and amide groups by amino acid residues may permit formation of the 1:4 hydrogen bond present in the *cis*-proline turn. The energy thus obtained may compensate for the loss of the 1:3 hydrogen bond.

In conclusion, ab initio calculations have shown that *N*-acetylproline amide forms the 1:3 hydrogen bond found in the γ turn. The energy of the hydrogen bond is estimated to be 3.7 kcal/mol. The cis conformation **3d** of *N*-acetylproline amide is higher in energy than the 1:3 hydrogen-bonded trans conformation **3a** by 4.1 kcal/mol and higher than the trans conformation **3b** with no hydrogen bond by only 0.4 kcal/mol. This last result agrees well with the results of the molecular mechanics calculations of DeTar and Luthra[3] for the cis and trans conformations of *N*-acetylproline methyl ester, which cannot form a hydrogen bond. It also agrees with the result of Pullman et al., who find a 0.5 kcal/mol stability of the trans non-hydrogen-bonded isomer over the cis isomer.

It is clear that the ab initio calculations at the STO-3G level are able to identify the structure C_7 as the most stable, being a global minimum on the energy hypersurface even though the puckering of the proline ring is underestimated.

Acknowledgment. We thank Lori E. Witterschein for excellent editorial assistance. This work was supported by a research contract from the Office of Naval Research and the Army Research Office.

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Electrostatic Potentials and Relative Bond Strengths of Some Nitro- and Nitrosoacetylene Derivatives

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Abstract: A computational analysis of the structures and properties of a group of substituted acetylenes has been carried out by means of an ab initio self-consistent-field molecular orbital procedure (GAUSSIAN 82). The molecules studied were acetylene, its singly and doubly substituted nitro and nitroso derivatives, methylnitroacetylene, and aminonitroacetylene. The properties computed were the molecular electrostatic potentials and the bond orders, used as measures of relative bond strengths. Among the interesting structural features found for these molecules are a slight nonlinearity of the $C{\equiv}C{-}N$ portions of mono- and dinitrosoacetylene and the fact that the two substituents in dinitro- and dinitrosoacetylene are not coplanar but rather lie in perpendicular planes. The presence of NO_2 is observed to strengthen the $C{\equiv}C$ bond, whereas NO substitution weakens it. The combination of NO_2 and NH_2 (a strong electron donor) has an overall weakening effect, relative to acetylene. The $C-NO_2$ bonds are found to be stronger than the C–NO bonds. The electrostatic potential analyses show that the introduction of NO_2 completely eliminates the negative regions associated with the triple bond, thus rendering it less susceptible to electrophilic attack. There are found to be buildups of positive potential above the $C-NO_2$ bonds, indicating that these can serve as initial sites for nucleophilic attack.

Substituted acetylenes, $R{-}C{\equiv}C{-}R'$, are of considerable interest as potential precursors in a variety of useful syntheses; e.g., cycloadditions with carbenes, olefins, and other acetylene derivatives yield small ring systems, while Diels–Alder reactions with cyclic dienes can lead to aromatic and cage-type molecules.[1,2] Depending upon the choice of substituents R and R′, a wide range of products can, in principle, be obtained. It is important, therefore, to understand how the reactive properties of $R{-}C{\equiv}C{-}R'$ are affected by the natures of R and R′.

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(1) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; Chapter 15.

(2) Bastide, J.; Henri-Rousseau, O. *The Chemistry of the Carbon-Carbon Triple Bond*, Part 1; Patai, S., Ed.; John Wiley & Sons: New York, 1978; Chapter 11.

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Table I. Calculated Structures[a]

molecule	energy (6-31G), hartrees	distances, Å		angles, deg	
$H-C\equiv C-H$	−483.4118	$C\equiv C$	1.194 (1.207)	$C\equiv C-H$	180.0 (180.0)
(I)		C—H	1.053 (1.058)		
$H-C\equiv C-NO$	−205.3413	$C\equiv C$	1.193	$C\equiv C-N$	175.2
(II)		C—N	1.376	C—N—O	116.8
		C—H	1.054		
		N—O	1.208		
$ON-C\equiv C-NO$	−333.8864	$C\equiv C$	1.196	O—N—C	118.3
(III)[b]		C—N	1.365	$N-C\equiv C$	173.4, 173.5
		N—O	1.206		
$H-C\equiv C-NO_2$	−280.1112	$C\equiv C$	1.186	$C\equiv N-O$	117.4, 117.5
(IV)		C—N	1.383	O—N—O	125.1
		C—H	1.054	$C\equiv C-N$	180.0
		N—O	1.226	$H-C\equiv C$	180.0
$O_2N-C\equiv C-NO_2$	−483.4131	$C\equiv C$	1.178	$C\equiv C-N$	180.0
(V)[b]		C—N	1.388	C—N—O	116.8
		N—O	1.223	O—N—O	126.4
$H_2N-C\equiv C-NO_2$	−335.1329	$C\equiv C$	1.194	$C\equiv C-NH_2$	180.0
(VI)		$C-NO_2$	1.364	C—N—H	120.9
		$C-NH_2$	1.318	H—N—H	118.2
		N—O	1.233	$C\equiv C-NO_2$	180.0
		N—H	0.992	O—N—O	124.4
				C—N—O	117.8
$H_3C-C\equiv C-NO_2$	−319.1477	$C\equiv C$	1.188	$C\equiv C-N$	180.0
(VII)		C—N	1.379	C—N—O	117.6
		C—C	1.460	O—N—O	124.7
		N—O	1.228	$C\equiv C-C$	180.0
		C—H	1.082	C—C—H	110.3–110.8

[a] All structures were optimized at the 6-31G level. [b] The 6-31G energy differences between the planar and nonplanar forms of III and V are 4.0 and 0.82 kcal/mol, respectively.

With this objective, we have carried out a computational analysis of a group of mono- and disubstituted acetylenes. The substituents included the CH_3, NO, NO_2, and NH_2 groups. We have focused in particular upon relative bond strengths, as predicted by a recently presented bond energy–bond order relationship,[3] and molecular electrostatic potentials.[4-6] The latter property is well established as a guide to the reactive behavior of molecules, as shall be discussed in the next section.

Methods

1. **General Approach.** The molecules that have been studied are acetylene itself (I), taken as a reference point, and the following six derivatives:

$$\underset{\text{II}}{H-C\equiv C-NO} \qquad \underset{\text{III}}{ON-C\equiv C-NO} \qquad \underset{\text{IV}}{H-C\equiv C-NO_2}$$

$$\underset{\text{V}}{O_2N-C\equiv C-NO_2} \qquad \underset{\text{VI}}{H_2N-C\equiv C-NO_2}$$

$$\underset{\text{VII}}{H_3C-C\equiv C-NO_2}$$

For each molecule, the initial step was to compute an optimized geometry with the ab initio self-consistent-field GAUSSIAN 82 program[7] at the 6-31G level. (This was done even in those instances in which an experimentally determined structure is available in order to ensure consistency in making comparisons.)

This optimum 6-31G geometry was used in calculating the bond orders and the electrostatic potentials. For the former, the STO-3G basis set was used; extensive tests have shown that the bond orders obtained at this level have very nearly the same *relative* magnitudes as do the 6-31G values.[8] The electrostatic potentials were computed with STO-5G basis sets; minimum basis ab initio SCF procedures have been shown to be generally reliable for determining this property.[4,5,9-11]

2. **Bond Orders.** We have recently demonstrated that experimentally measured bond dissociation energies correlate well with bond orders calculated by means of eq 1.[3] k and R_e are the force constant (in

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

mdyn/Å) and equilibrium bond length (in Å), respectively, both of which can be computed with the GAUSSIAN 82 program. Equation 1 represents a practical means for predicting the relative strengths of chemical bonds, particularly when it is a given type of bond (e.g., $C\equiv C$) in different environments.

3. **Electrostatic Potentials.** The electrostatic potential that is created at any point $\vec{r}$ in the space around a molecule by its nuclei and electrons is given rigorously by eq 2. Z_A is the charge on nucleus A, located at

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')\,d\vec{r}'}{|\vec{r}' - \vec{r}|} \qquad (2)$$

$\vec{R}_A$, and $\rho(\vec{r})$ is the electronic density function of the molecule, which we obtain from our computed molecular wave function.

The electrostatic potential is a real physical property, which can be determined experimentally as well as computationally.[6] It has proven to be an effective means for interpreting and predicting the reactive properties of molecules, particularly toward electrophiles.[4-6] An approaching electrophile will initially be attracted to those regions in which $V(\vec{r})$ is negative, since these are where the effects of the molecule's electrons are dominant, especially at those points at which $V(\vec{r})$ has its most negative values (the local minima).

Results and Discussion

1. **Structures.** Our calculated geometries for the molecules studied in this work are given in Table I. A particularly striking feature of these is the nonplanarity of dinitrosoacetylene (III) and dinitroacetylene (V). In III, the dihedral angle between the two

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(3) Politzer, P.; Ranganathan, S. *Chem. Phys. Lett.* **1986**, *124*, 527–530.

(4) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 115–193.

(5) Politzer, P.; Daiker, K. C. *The Force Concept in Chemistry*; Deb, B. M., Ed.; Van Nostrand-Reinhold: New York, 1981; Chapter 6.

(6) Politzer, P.; Truhlar, D. G., Eds. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press: New York, 1981.

(7) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A., GAUSSIAN 82, Release A, Carnegie-Mellon University.

(8) Elminyawi, I.; Kirschenheuter, G. P.; Murray, J. S., private communication.

(9) Scrocco, E.; Tomasi, J. *Topics in Current Chemistry*, Springer-Verlag: Berlin, 1973; No. 42, p 95.

(10) Ghio, C.; Tomasi, J. *Theor. Chim. Acta* **1973**, *30*, 151–158.

(11) Almlof, J.; Stogard, A. *Chem. Phys. Lett.* **1974**, *29*, 418–420.

Table II. Calculated Bond Orders

molecule	bond	bond order
H—C≡C—H (I)	C≡C	2.42
	C—H	1.60
H—C≡C—NO (II)	C≡C	2.41
	C—N	1.37
	C—H	1.60
	N—O	2.29
ON—C≡C—NO (III)	C≡C	2.34
	C—N	1.39
	N—O	2.29
H—C≡C—NO_2 (IV)	C≡C	2.47
	C—N	1.45
	C—H	1.60
	N—O	2.05
O_2N—C≡C—NO_2 (V)	C≡C	2.54
	C—N	1.41
	N—O	2.07
H_2N—C≡C—NO_2 (VI)	C≡C	2.38
	C—NO_2	1.52
	C—NH_2	1.67
	N—O	2.00
	N—H	1.85
H_3C—C≡C—NO_2 (VII)	C≡C	2.45
	C—N	1.46
	C—C	1.27
	N—O	2.04
	C—H	1.48

C-C-O planes is 87°, while in V the two NO_2 groups are in perpendicular planes. Resonance considerations suggest that these configurations are adopted because they permit each substituent group to conjugate with one of the π bonds of the carbon–carbon triple bond, producing an additional stabilization of the system. Thus, even though the tendency of the NO_2 group to conjugate with a π system is believed to be slight,[12] and has indeed been the subject of some recent controversy,[13-15] the structures that we have obtained for III and V suggest that the opportunity for conjugation is a significant factor for both the nitro and the nitroso groups.[16] (It is very interesting to note that despite the apparent importance of conjugation in determining the geometry of dinitroacetylene, the properties that are being investigated in this work—bond orders and electrostatic potential—were found to be virtually the same whether the nitro groups are coplanar or in perpendicular planes. It is the considerable inductive power of NO_2 that does appear to be a major influence on these properties.)

All of the other molecules studied in this work were found to be planar (except for the methyl hydrogens in VII). The coplanarity of the NH_2 group in VI with the rest of the molecule is fully anticipated when it is combined with the strongly electron-withdrawing (by induction) NO_2 group, since it is in the planar configuration that NH_2 is most effective as a resonance π donor.[17,18]

A noteworthy aspect of the structures of both mono- and dinitrosoacetylene, II and III, is the nonlinearity of the C≡C—N portions of these molecules. The C-C-N angles are 175° and 173°, respectively, rather than the 180° that would be anticipated for sp-hybridized carbons. While such departures from linearity are rather unusual for sp systems, they do occur on occasion; an example is tetracyanoethylene, in which the C-C-N angle has been shown by neutron diffraction to be 178°.[19]

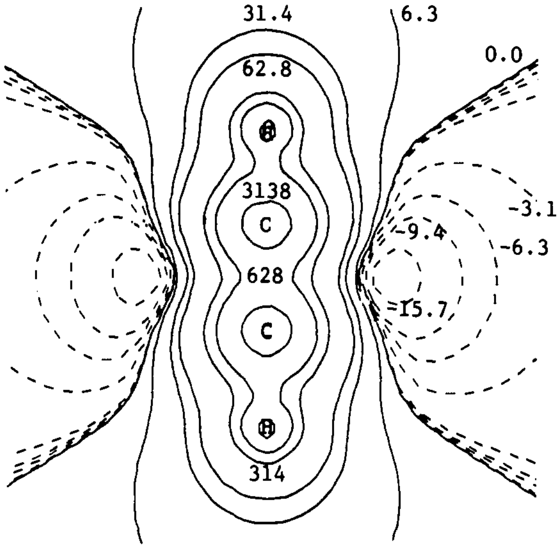
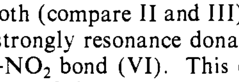


Figure 1. Calculated electrostatic potential in a plane through the molecular axis of acetylene. The positions of the nuclei are indicated. Dashed contours represent negative potentials. All values are in kcal/mol.

2. Bond Orders. The calculated bond orders are presented in Table II. As discussed earlier, these shall be taken as measures of the relative strengths of bonds of a given type. For example, these data indicate that the C-H bonds in acetylene, nitrosoacetylene, and nitroacetylene should have very similar bond energies, stronger than more typical C-H bonds such as those of the methyl group in 1-methyl-2-nitroacetylene. This would be fully consistent with the well-known strengthening effect that multiple bonds have on adjacent single bonds.[20,21]

It is interesting to observe that the nitro and nitroso groups have opposite effects upon the strength of the C≡C bond. This can be seen by taking acetylene as the reference point and then comparing the bond orders in the pairs II, III and IV, V. Substitution of the nitro group clearly strengthens the C≡C bond, whereas the nitroso weakens it. It is important to note, however, that when NO_2 is present along with a group that is a strong electron donor (through resonance), such as NH_2, the overall result is a weakening of the C≡C bond (relative to acetylene), as is shown for VI. This weakening can be rationalized by invoking the resonance structure VIII. A weak donor, such as CH_3 (VII), causes the C≡C bond to be weaker than that in nitroacetylene but still stronger than that in acetylene itself.



VIII

Another point that is brought out by Table II is that the C-NO_2 bonds are consistently stronger than the C-NO bonds. It is noteworthy, however, that the substitution of a second NO_2 weakens both C-N bonds (compare IV and V), while a second NO strengthens both (compare II and III). On the other hand, the effect of the strongly resonance donating NH_2 group is to strengthen the C-NO_2 bond (VI). This can perhaps again be rationalized in terms of the resonance structure VIII.

A final interesting feature of Table II is that the nitroso N-O bonds are invariably stronger than those in the nitro groups. This can readily be explained, in resonance terms, by noting that the

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[12] Evidence of this is given by the rather small magnitude of the Taft substituent constant σ_R for NO_2. See, for example: Wells, P. R. *Linear Free Energy Relationships*; Academic Press: New York, 1968; Chapter 2.

[13] Lipkowitz, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 2647–2648.

[14] Fraser, R. R.; Raganskas, A. J.; Stothers, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 6475–6476.

[15] Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1984**, *106*, 6963–6968.

[16] We are greatly indebted to Dr. Jane S. Murray and Dr. Robert T. Patterson for very helpful discussions and suggestions concerning these points.

[17] Politzer, P.; Abrahmsen, L.; Sjoberg, P. *J. Am. Chem. Soc.* **1984**, *106*, 855–860.

[18] Politzer, P.; Jayasuriya, K.; Zilles, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 121–124.

[19] Becker, P.; Coppens, P.; Ross, F. K. *J. Am. Chem. Soc.* **1973**, *95*, 7604–7609.

[20] Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166–178. Wilson, E. B., Jr. *Tetrahedron* **1962**, *17*, 191–198.

[21] Politzer, P.; Harris, R. R. *Tetrahedron* **1971**, *27*, 1567–1572.

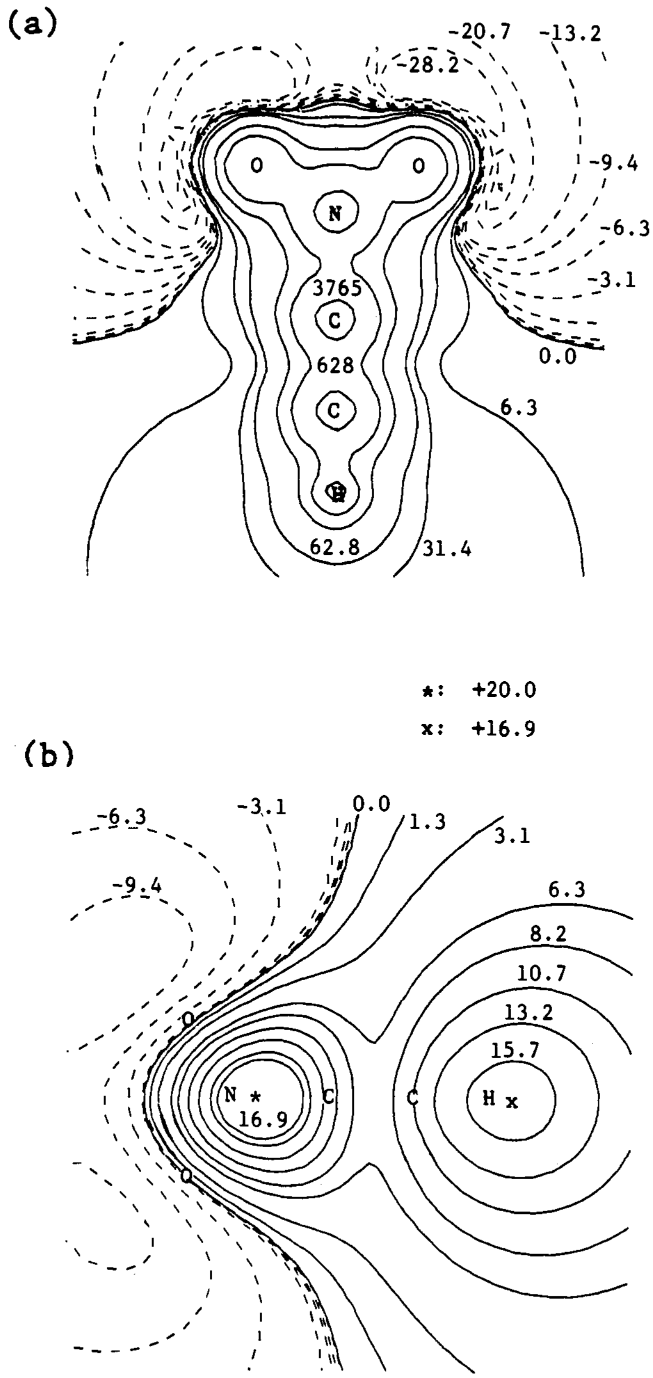
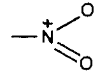
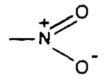
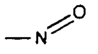


Figure 2. Calculated electrostatic potentials of nitroacetylene (IV) in the molecular plane (a) and 1.75 Å above the molecular plane (b). The positions of the nuclei are indicated. Dashed contours represent negative potentials; all values are in kcal/mol. In part b, the locations of the planar maxima are shown by * and x, and their magnitudes are given above the figure.

nitro group is commonly represented by the structures IX and X and the nitroso by structure XI. There is no likely resonance


IX


X


XI

contributor to NO_2 in which there are simultaneously double bonds to both oxygens.[22]

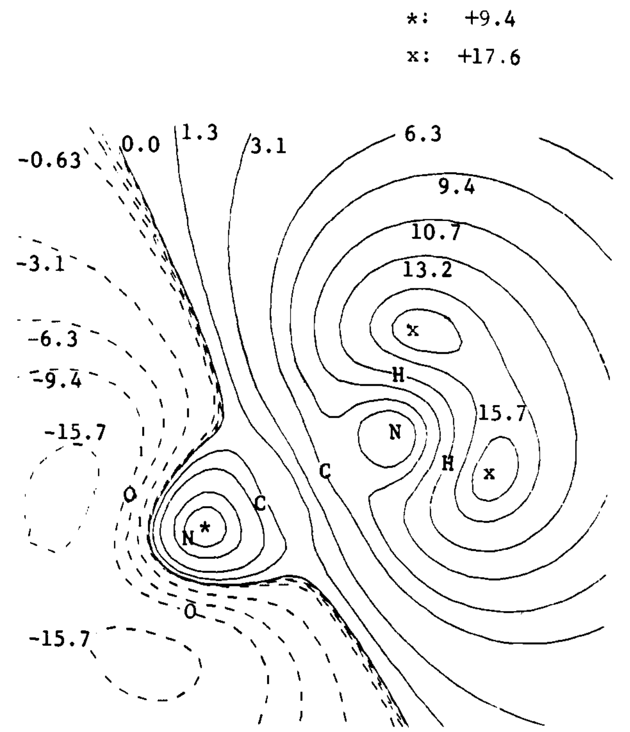


Figure 3. Calculated electrostatic potential of aminonitroacetylene (VI) 1.75 Å above the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potentials; all values are in kcal/mol. The locations of the planar maxima are shown by * and x, and their magnitudes are given above the figure.

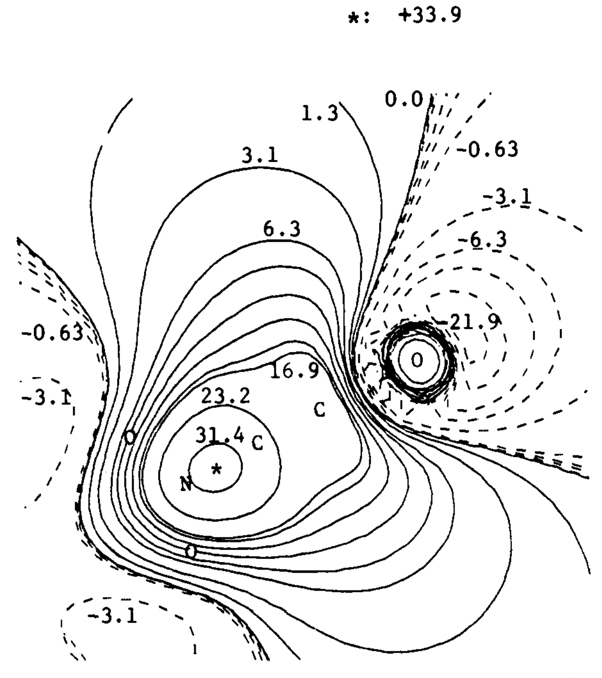


Figure 4. Calculated electrostatic potential of dinitroacetylene (V) 1.75 Å above the $C{\equiv}C{-}NO_2$ plane. (One NO_2 group is perpendicular to this plane.) The positions of the nuclei are indicated. Dashed contours represent negative potentials; all values are in kcal/mol. The location of the planar maximum is shown by *, and its magnitude is given above the figure.

3. Electrostatic Potentials. In Table III are reported the magnitudes and locations of the most negative electrostatic potentials (the local minima) that are associated with each molecule. Some representative plots of the potential are shown in Figures 1-5.

Looking first at acetylene, the parent molecule, the distinctive feature of its electrostatic potential is a large cylindrically sym-

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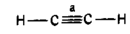
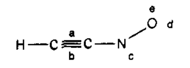
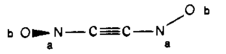
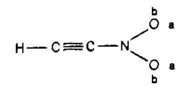
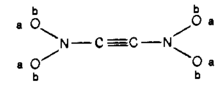
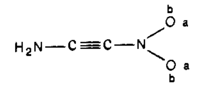
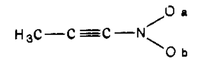
[22] Both the calculated structure and the bond orders of dinitroacetylene, (III) support describing it as $O{=}N{-}C{\equiv}C{-}N{=}O$, contrary to an alternative view of it as a di-*N*-oxide: $O^{-}{-}N^{+}{\equiv}C{-}C{\equiv}N^{+}{-}O^{-}$ [Grundmann, C. J.; Mini, V.; Dean, J. M.; Frommeld, H. D. *Ann. Chem.* **1965**, *687*, 191-214].

Table III. Summary of Calculated Electrostatic Potentials[a]

molecule	approx locations of potential min.	values of minima		values of planar maxima[b]	
$H—C\equiv C—H$ (I)		a:	−19.8	H:	+4.0
$H—C\equiv C—NO$ (II)		a: b: c: d: e:	−5.5 −8.1 −57.3 −34.7 −25.5	H:	+10.7
$ON—C\equiv C—NO$ (III)		a: b:	−46.7 −28.5	C—NO:	+14.3
$H—C\equiv C—NO_2$ (IV)		a: b:	−47.3 −39.8	H: $C—NO_2$:	+16.9 +20.0
$O_2N—C\equiv C—NO_2$ (V)		a: b:	−35.0 −26.1	$C—NO_2$:	+35.0
$H_2N—C\equiv C—NO_2$ (VI)		a: b:	−58.6 −49.9	$C—NO_2$:	+9.4
$H_3C—C\equiv C—NO_2$ (VII)		a: b:	−52.1 −52.0	$C—NO_2$:	+8.3

[a] All values are in kcal/mol. [b] See text for more detailed discussion of the locations of these maxima.

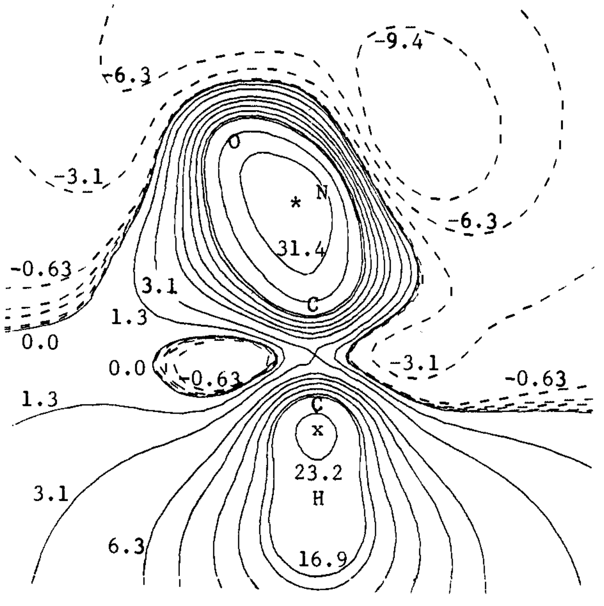


Figure 5. Calculated electrostatic potential of nitrosoacetylene (II) 1.75 Å above the molecular plane. The positions of the nuclei are indicated. Dashed contours represent negative potentials; all values are in kcal/mol. The locations of the planar maxima are shown by * and x, and their magnitudes are given above the figure.

metrical negative region that reaches its greatest magnitudes near the midpoint of the $C\equiv C$ bond (Figure 1). It would therefore be predicted that this is the favored site for initial interaction with an electrophile. This has indeed been found to be the case, in the protonation of acetylene,[23] the formation of π-complexes and hydrogen bonds,[24] and various other reactions with electrophiles.[25] The magnitude of this most negative potential, −19.8 kcal/mol, is significantly more negative than the corresponding value for ethylene, −13.1 kcal/mol,[26] as would be expected in going from a double to a triple bond.

The large negative region associated with the triple bond of acetylene is completely eliminated by the substitution of the nitro group (Figure 2). Even the NH_2 portion of VI is left without a negative potential, which it normally would have (Figure 3).[18] All this can be attributed to the very strong inductive electron-withdrawing power of the NO_2. It has been observed to have the same type of effect—elimination of negative regions associated with the carbon framework—in a variety of other systems, including strained,[27,28] aromatic,[17] and heterocyclic[29] molecules. Thus, the presence of the NO_2 group should significantly diminish the susceptibility of the $C\equiv C$ bond to electrophilic attack.

The nitroso group apparently has much less inductive power, since nitrosoacetylene (II) retains a negative potential near the $C\equiv C$ bond, although it is considerably weaker than in acetylene (Table III). However, two substituted nitroso groups do suffice to eliminate the negative $C\equiv C$ potential.

Unlike the nitrogen in the NO_2 group, the nitroso nitrogen does have a relatively localized lone pair and corresponding strong negative electrostatic potential. It is clearly a likely site for electrophilic attack. The oxygens, on the other hand, are more negative in the nitro group than in the nitroso; this can be attributed in part to the resonance structures IX and X, but the strong inductive power of the NO_2 group must also play an important role. The significance of this factor can be seen by comparing the oxygen minima in nitroacetylene (−47.3 and −39.8 kcal/mol) with those in nitrobenzene (−56.7 and −42.8 kcal/mol).[17] The difference is consistent with the greater polarizability of benzene (12.31×10^{-24} cm^3) compared to acetylene (5.12×10^{-24} cm^3)[30] and can be interpreted as indicating that the NO_2 group is able to achieve a greater degree of inductive polarization in nitrobenzene than in nitroacetylene.

A general pattern that is followed by both the nitro and nitroso derivatives, II–V, is that the negative potentials associated with the substituents become weaker in going from the mono- to the disubstituted molecule. This simply reflects the fact that in the latter instances there are two electron-withdrawing groups competing for the polarizable electronic charge, and hence each of them can be expected to receive less of it. The same situation

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(30) Ross, S.; Olivier, J. P. *On Physical Adsorption*; John Wiley & Sons: New York, 1964, Table VI-2. The values cited are the polarizability in the plane of the ring for benzene and along the molecular axis for acetylene.

has been observed earlier in other systems.[26,31] As would be anticipated, the opposite is observed to occur when a nitro group is combined with a second substituent that is an electron donor, such as NH_2 (VI) or, to a lesser extent, CH_3 (VII); the potentials associated with the oxygens are then considerably more negative than in nitroacetylene (IV).

There are also certain aspects of the positive electrostatic potential regions of these molecules that are of considerable interest. Among these are the buildups of positive potential that are found above the $C-NO_2$ bond regions in the four nitroacetylenes. Positive buildups are generally associated with nuclei; it is rather unusual, and noteworthy, to find them elsewhere, especially above bonds. This feature can be seen in Figures 2b, 3 and 4.

The magnitudes of the positive $C-NO_2$ potentials depend upon the nature of the other substituent (Table III). When the latter functions as an electron donor (e.g., NH_2 and CH_3), this positive region is weakened; however, electron-withdrawing groups, such as NO and NO_2, considerably strengthen it.

We have earlier found similar positive regions to be associated with the $C-NO_2$ bonds of a number of nitroaromatics, including some heterocyclic systems.[17,29,32] It was shown that these regions could be related to the tendencies of the molecules to undergo nucleophilic attack upon the $C-NO_2$ bonds.[32] The same can be predicted for these nitro-containing acetylene derivatives, especially dinitroacetylene (V), which has the strongest positive buildup that we have yet observed.[33]

The nitrosoacetylenes (II and III) also show some rather intriguing positive regions, above the C-N-O angles and above the C-H bond (Figure 5). Finally, it is interesting to note the buildups of positive potential near the hydrogens in $H-C\equiv C-H$, $H-C\equiv C-NO_2$, and $H_2N-C\equiv C-NO_2$. The significance of these various positive regions (e.g., a possible relationship of the latter group to acidity and hydrogen-bonding ability[24]) is presently being investigated.

Summary

Among the results of this study are several points that may have considerable bearing upon the potential usefulness of nitroso- and nitroacetylenes as precursors in synthesis. Of particular importance are the effects of these two substituents—NO and NO_2—upon the $C\equiv C$ bond. The presence of the nitro group, in itself, strengthens this bond; NO substitution, on the other hand, weakens it. A key observation, however, is that the combination of NO_2 with NH_2, a strong electron donor, has an overall weakening effect (relative to acetylene).

It is also of interest to note that while the $C-NO_2$ bonds are stronger than the C-NO, the former become weaker in going from mono- to dinitroacetylene, whereas the latter are stronger in dinitrosoacetylene than in the singly substituted derivative.

In addition to these determinations of relative bond strengths, which were obtained by means of bond order calculations, we have examined how the electrostatic potentials of these molecules are affected by the various substituents. One general result is that the strong negative potential associated with the triple bond of acetylene is entirely eliminated by the introduction of even *one* nitro group. This is fully consistent with previous observations of the effect of this substituent and indicates a diminished susceptibility of the $C\equiv C$ bond toward electrophilic attack. The NO group has a lesser influence upon the triple bond potential, but in the dinitroso derivative, the latter is again completely positive.

Other significant features of these molecules include the buildups of positive potential that are found above the $C-NO_2$ bond regions. These are believed to indicate the possibility of the $C-NO_2$ bond serving as an initial site for nucleophilic attack.

There are certain particularly interesting aspects of the structures of some of these molecules. These include the slight nonlinearity of the $C\equiv C-N$ portions of mono- and dinitrosoacetylene and, perhaps more important, the nonplanarity of dinitro- and dinitrosoacetylene. The two substituents in these latter molecules are found to be in perpendicular planes, presumably to allow each to conjugate individually with one of the $C\equiv C$ π bonds.

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Bonding and Polymerization Mechanism of Substituted Tetramethylenes

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Abstract: The polymerization mechanism of tetramethylenes is studied with a recently developed concept of valence numbers. It is shown that the diradical mechanism prevails for small bond number differences between zwitterionic and diradical states, whereas the zwitterionic mechanism is characterized by large bond number differences. A comparison of SINDO1 calculations for 10 selected substituted tetramethylenes shows good agreement with the trend of experimental data. The calculations establish a scale for the prediction of the polymerization mechanism of donor-acceptor substituted tetramethylenes.

I. Introduction

Recently important progress was made in the explanation of the bond-forming initiation in spontaneous addition and polymerization reactions of alkenes. In a survey of a vast amount of experimental data Hall[1] suggested the investigation of the properties of *trans*-tetramethylenes to predict the polymerization mechanism. His work is based on the conclusion drawn by Salem and Rowland[2] that there are pairs of 1,4-diradical (DR) and

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