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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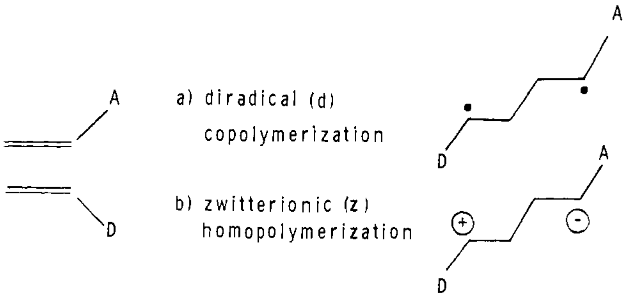

Figure 1. Polymerization mechanisms of tetramethylenes.

1,4-zwitterionic (ZI) states of tetramethylene. These are stabilized relative to each other dependent on the substituents of the reacting ethylenes. Huisgen, who has long been involved with the kinetic proof of reactive intermediates,[3] has particularly addressed himself to the question of trapping tetramethylenes.[4] The emphasis of this work was on the 1,4-dipolar cycloadditions of zwitterionic intermediates. Trapping provides evidence for the existence of an intermediate. Hall has used these ideas, but he has gone beyond them significantly. He finds that an effective way of trapping an intermediate is to initiate polymerization. The advantages are (a) the amplification of a small amount of reactive species that will lead by chain reaction to an easily detectable yield of polymer and (b) diagnosis of the diradical and zwitterionic nature of the tetramethylene by the structure of the polymer. Homopolymers of either one or both alkenes should indicate the existence of a 1,4-zwitterionic intermediate because such intermediates avoid polymerization and react fast to dimers. On the other hand, alternating copolymers could be formed from diradical intermediates of tetramethylene. This idea is presented in Figure 1. A highlight in Hall's paper[1] is a diagram predicting the diradical or zwitterionic mechanism depending on donor and acceptor ability of the reacting alkenes. More recently Gotoh and Hall[5] have investigated the polymerization reactions of *N*-vinylcarbazole with seven electrophilic tetrasubstituted olefins containing cyano and/or carbomethoxy groups. Left in excess *N*-vinylcarbazole solution, the olefins or the corresponding cyclobutane cycloadducts initiated homopolymerization of *N*-vinylcarbazole. This is interpreted as a consequence of zwitterionic form of the tetramethylene intermediates.

In this paper a study of 10 substituted tetramethylenes is presented which predicts the diradical or zwitterionic mechanism by using a newly developed valence concept.

II. Valence and Bond Numbers

We have recently developed a valence criterion for diradicals and zwitterions.[6] This was based on a definition of valence numbers of atoms in molecules[7,8] to measure the amount of used covalent bonding capacity of atoms in molecules.

We start from an expansion of the molecular orbitals (MOs) ψ_i in a set of symmetrically orthogonalized atomic orbitals λ_μ[9]

$$\psi_i = \sum_{\mu} c_{i\mu}\lambda_\mu \tag{1}$$

From the coefficients $c_{i\mu}$ of the occupied (occ) MOs the usual first-order reduced density matrix is constructed

$$P_{\mu\nu} = \sum_{i}^{\text{occ}} n_i c_{i\mu} c_{i\nu} \tag{2}$$

where n_i is the occupation number of the MO ψ_i. On the configuration interaction (CI) level with double excitations fractional occupancy will arise in general. For coupling between singly and doubly excited configurations the natural orbitals (NOs) and their corresponding occupation numbers should be used in (1) and (2).

It was demonstrated previously[7,8] that the covalent bonding between a pair of atoms A and B can be measured by the *bond valence* V_{AB}

$$V_{AB} = \sum_{\mu,\nu} P_{\mu_A\nu_B}{}^2 \tag{3}$$

The *atomic valence* is the sum of contributions from all other atoms to a reference atom. The atomic valence number is then defined as

$$V_A = \sum_{B\neq A} V_{AB} \tag{4}$$

Finally, the total number of covalent bonds can be characterized by the *bond number* M[8] as

$$M = \tfrac{1}{2}\sum_{A} V_A \tag{5}$$

The standard normal valence number V of carbon atoms is 4, of nitrogen atoms 3, and of oxygen atoms 2. In normal neutral molecules like CH_4, NH_3, or H_2O the actual valence numbers are very close to these standard integer values. Hypervalent atoms are characterized by increased valence numbers above the standard value and subvalent atoms by decreased valence numbers below the standard value. Diradicals and zwitterions contain subvalent atoms. In tetramethylenes a reduction of valence numbers will be observed in particular at the donor and acceptor carbon atoms both for diradical and zwitterionic states. In the diradical case the molecule contains one bond less than allowed by standard rules of valence.[10] Correspondingly the total reduction of valence numbers at the diradical sites is about 2 compared to the normal values. In the zwitterionic case the charge transfer from one atom or one group to another reduces the MO coefficients at the donor site and increases the MO coefficient at the acceptor site. This leads to an overall reduction of the product of MO coefficients of the different sites which is a measure of covalent bonding. Since there is only partial charge transfer in a zwitterion, the reduction of valence numbers should be less pronounced than that for a diradical. The total covalent bonding in a molecule can be characterized by the bond number M which is the half-sum of all atomic valence numbers according to eq 5.[8] Since there is one bond less than allowed by the rules of valence in a diradical of tetramethylene structure, M is reduced by approximately one unit from the normal value for a diradical and usually less for a zwitterion. In this sense, the bond number seems to be well-suited to distinguish between diradical and zwitterionic states of tetramethylenes. In addition, the charge distribution and dipole moment can be used because charge separation is larger in the zwitterions.

III. Results and Discussion

For the calculations we have used the semiempirical MO method SINDO1[11] whose accuracy was comprehensively established for geometries and binding energies of compounds with first-row elements.[12] For the present purpose it should be pointed out that the accuracy of SINDO1 was also established on the configuration interaction level. In a study on the cycloreversion of cyclobutanes[13] we found an energy barrier of 70.1 kcal/mol for the unsubstituted case. This compares favorably with the experimental value of 62.5 kcal/mol.[14] If we take into account that the SINDO1 binding energy of cyclobutane is 9.4 kcal/mol too low, the calculated energy barrier is of good accuracy. An early ab initio calculation of Segal[15] arrived at a barrier of 73.0 kcal/mol. More recently ab initio calculations concentrated on the singlet–triplet energy gap of tetramethylenes.[16] The splitting was calculated in the order of 1 kcal/mol. A 4 × 4 CI of SINDO1 yields only a fraction of a kcal/mol.

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Table I. Geometry (Å, deg) of Carbon Fragments of Tetramethylenes with Diradical (d) and Zwitterionic (z) Ground State

			geometry[a]				
donor	acceptor	type	C_1C_2	C_2C_3	C_3C_4	$C_1C_2C_3$	$C_2C_3C_4$
H	H	d	1.493	1.565	1.493	118.2	118.2
H	CN	d	1.499	1.564	1.509	117.1	118.6
4F	CN	d	1.541	1.607	1.506	112.6	116.0
OCH_3	4F	d	1.498	1.574	1.574	118.1	118.2
C_6H_5	CN	d	1.499	1.570	1.481	116.7	120.8
OCH_3	2CN	d	1.524	1.558	1.502	110.4	123.5
OCH_3	NO_2	d	1.503	1.560	1.479	116.2	126.1
$2CH_3$, NH_2	2CN	z	1.550	1.690	1.573	110.9	118.4
$2OCH_3$	$COOCH_3$	z	1.628	1.585	1.514	108.6	110.8
$2CH_3$, NH_2	$COCH_3$	z	1.567	1.676	1.521	109.7	114.7

[a] C_1 donor carbon, C_4 acceptor carbon.

Table II. Total Energy (E) and Bond Number (M) Changes between Zwitterionic (z) and Diradical (d) States and LUMO–HOMO Energy Differences of Ground States S_0

molecule				
donor (D)	acceptor (A)	$E_z - E_d$ (hartree[a])	$M_z - M_d$	$\epsilon_{LUMO} - \epsilon_{HOMO}$ (hartree[a])
H	H	0.38	0	0.007
H	CN	0.34	0	0.009
4F	CN	0.32	0.09	0.006
OCH_3	4F	0.27	0.01	0.013
C_6H_5	CN	0.22	0.01	0.018
OCH_3	2CN	0.19	0.11	0.034
OCH_3	NO_2	0.09	0.23	0.090
$2CH_3$, NH_2	2CN	−0.05	0.71	0.173
$2OCH_3$	$COOCH_3$	−0.06	0.69	0.187
$2CH_3$, NH_2	$COCH_3$	−0.06	0.73	0.176

[a] 1 hartree = 627.46 kcal/mol.

Finally the CI version of SINDO1 is also capable of dealing with rotation barriers about double bonds. The barrier of rotation for ethylene is 67 kcal/mol compared to 65 kcal/mol experimentally.[17] We have performed SINDO1 calculations including a 4 × 4 configuration interaction (CI) to optimize the trans configuration of 10 selected tetramethylenes. The tetramethylene framework was kept planar, but all other internal coordinates were varied to minimize the energy of the ground states S_0. At the same time the energy of the excited states S_1 was calculated. No separate optimization of S_1 was attempted since no more pertinent information on the mechanism could be obtained. These states were analyzed for their diradical and zwitterionic character.

The geometries of the tetramethylene ground states S_0 are listed in Table I. No general pattern evolves except that the inner bond length is usually longer than the outer bond lengths and that the CCC bond angle at the donor site is smaller than that at the acceptor site.

Much more informative are the results of Table II. Here the differences in total energies and in bond numbers between diradical and zwitterionic states are presented. Positive energy differences indicate that the diradical state of the tetramethylene is more stable than that of the zwitterionic states. So we find seven diradical and three zwitterionic ground states. The decrease of energy differences is accompanied by an increase in bond number difference $M_z - M_d$. Large bond number differences indicate the dominant stability of the zwitterionic state. To see the trend one could also compare molecular orbital (MO) energy differences of lowest unoccupied (LUMO) and highest occupied (HOMO) orbitals. The MO energies were calculated with a recently presented multiconfiguration formalism.[18] In this formalism there is a quasioccupation of the LUMO so that the orbital energy will be negative. This is a more physical situation than in the SCF method where a portion of the self-interaction of the excited electron is still retained.

If we were to conclude from the total energy data what the polymerization mechanism would be, we would suggest that the first seven proceed by a diradical-initiated mechanism, whereas the last three proceed by a zwitterion-initiated mechanism. If we compare these results with the diagram composed by Hall, we see the trend is in excellent agreement. But Hall's borderline zwitterion-initiated cases of compounds **6** and **7** turn out to be diradical initiated in our calculations. We suspect that solution effects could turn a gas phase borderline diradical situation into a zwitterionic one. Altogether it seems gratifying that theoretical and experimental data agree in the trend. We could extrapolate the initiation mechanism of the actual polymerization by defining a limit of bond number difference which separates the diradical and zwitterionic region. In this way a scale for the prediction of the pertinent mechanism of substituted donor–acceptor tetramethylenes can be established.

Acknowledgment. I am indebted to Prof. Hall for drawing my attention to the polymerization mechanism of tetramethylene and for a preprint of his paper. I also thank A. Rehr for the calculations of the compounds.

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