Solvation Effects on Diradicals and Zwitterions: Tetramethylenes and Trimethylenes

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Received: April 13, 1998

A solution model previously implemented in the semiempirical molecular orbital method SINDO1 is applied to the study of trimethylenes and tetramethylenes in different solvents. It is shown that diradical trimethylenes and tetramethylenes are polarized by the solvent. This influence of the solvent can also lead to a zwitterionic state in cases where a diradical is predicted without the solvent. Solution effects are the reason for the discrepancy between the experimentally observed polymerization mechanisms of substituted tetramethylenes and gas phase calculations. For a prediction of the correct state, a geometry optimization in solution is important.

I. Introduction

The first sound and generally accepted theoretical definition of diradicals and zwitterions was given by Salem and Rowland.[1] It is based on a four-state model including the single and double excitations from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This energy diagram considers singlet−triplet degeneracy and charge transfer. Alternatively, such a configuration interaction scheme can also be used to measure the valence of atoms in molecules. We have presented a theory of valence on the self consistent field (SCF) level,[2] on the configuration interaction (CI) level,[3] and on the natural orbital (NO) level.[4] On this basis, we introduced a valence reduction on two centers due to a broken bond as a criterion for diradicals and a valence reduction on one center accompanied by a valence increase on a second center due to charge transfer as criterion for zwitterions.[5] This scheme was later more rigorously defined on the NO level[6] and used a classification scheme for molecular systems. Much of the motivation for this theoretical development was drawn from experiment. Hall[7] had reviewed the literature on polymerization mechanisms of substituted tetramethylenes and had made an important observation. He found that the experimental facts could be explained if one assumes that copolymerization would be initiated by diradical intermediates and that homopolymerization takes place via zwitterionic intermediates. In a diagram, he illustrated how the donor and acceptor character of the substituents influences the character of the tetramethylene as diradical or zwitterion. In this way he could define substituent regions for occurrence of diradicals and zwitterions. We had subsequently tested this scheme by semiempirical MO calculated on 10 selected tetramethylenes.[8] We found basic agreement with Hall's prediction. But in two cases we found a diradical character of the substituted *trans*-tetramethylenes where zwitterionic character was predicted from the experimental results. To resolve this discrepancy, we claimed that the influence of the solvent, which was not included in the calculation, was the reason for the change from diradical to zwitterion. To substantiate this claim we performed a supermolecule calculation on one of the two systems, namely, 1-methoxy-4,4-dicyanotetramethylene, and simulated the solvent by a single methanol molecule. We could show that upon approach of the methanol

molecule to the carbon atom adjacent to the donor group OCH_3 the character switched from diradical to zwitterion.[9]

In the present paper we extend this idea to solvents in general. For this purpose we use the polarizable continuum model[10] (PCM) which has been recently implemented in the semiempirical molecular orbital method SINDO1.[11] This method has been successfully used on a wide range of chemical problems, ranging from organic photoreactions, aromaticity, properties of clusters, and crystal structures to heterogeneous catalysis. This work has been recently reviewed on the SCF and CI level.[12−14] The calculation of solvation energies for organic molecules and the comparison with experimental results showed that good accuracy can be achieved in this way.[15] In the following sections we present first the theory of diradicals and zwitterions and the solvation model. We then apply this model to the study of tetramethylenes and trimethylenes and show how the polarizability of the solvent influences the character of diradicals and zwitterions.

The influence of solvents on the electronic nature of 1,3-dipoles has been studied before also by ab initio techniques. Clark and co-workers[16] performed 6-31G* calculations on small 22- and 24-electron, 1,3-dipoles which were placed in solvents *n*-hexane, methanol, and water. The solvents were introduced as perturbation in the self-consistent reaction field approach.[10,17] It was shown that the zwitterionic form is stabilized by increasingly polar solvents, even though it is not always favored over the diradical form. The geometries taken were those of the gas phase. The change of weight of ionic and covalent forms of gas phase structures by solvents has been investigated by two other groups.[18,19] We found increasing weight of ionic forms with increasing solvent polarity.

The question of the behavior of 1,3-dipoles has also been analyzed ab initio in terms of basis sets. Hiberty and Ohanessian[20] found that there are no significant discrepancies between the structure weights of diradicals and zwitterionic forms with both minimal and extended basis sets. More important can be the effects of correlation on the charges.[21]

In order to justify the use of our formally minimal basis set method further two remarks are in order. SINDO1 atomic charges are not comparable with minimal basis set charges, rather the parametrization simulates more extended basis set

charges.[22] This is an additional reason why qualitatively safe statements on the reaction mechanism are to be expected.

II. Character of Diradicals and Zwitterions

On the basis of NOs ω_i which are expanded in symmetrically orthogonalized orbitals[23] (OAOs)

$$\omega_i = \sum_\mu a_{i\mu} \lambda_\mu \qquad (1)$$

density matrix elements of the first-order reduced density operator P are given by

$$P_{\mu\nu} = \sum_i n_i' a_{i\mu} a_{i\nu} \qquad (2)$$

where n_i' is the occupancy of the NO ω_i.[4] The valence of atomic orbital (AO) μ on atom A is defined as

$$V_\mu = \sum_{B \neq A}^{B} \sum_\nu (P_{\mu\nu})^2 = \sum_\nu P_{\mu\nu}^2 - P_{\mu\mu}^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2 \qquad (3)$$

Here μ, μ' are AOs on the same atom A and ν on a different atom. If we use the orthonormality of the NOs we can rewrite the first term in eq 3 as follows

$$\sum_\nu P_{\mu\nu}^2 = \sum_\nu \sum_i n_i' a_{i\mu} a_{i\nu} \sum_j n_j' a_{j\mu} a_{j\nu}$$

$$= \sum_i \sum_j n_i' n_j' a_{i\mu} a_{j\mu} \sum_\nu a_{i\nu} a_{j\nu}$$

$$= \sum_i \sum_j n_i' n_j' a_{i\mu} a_{j\mu} \delta_{ij}$$

$$= \sum_k (n_k' a_{k\mu})^2 \qquad (4)$$

We now define the orbital charge q_μ as

$$q_\mu = P_{\mu\mu} \qquad (5)$$

and the contribution $q_{i\mu}$ of NO ω_i to the orbital charge q_μ as

$$q_{i\mu} = n_i' (a_{i\mu})^2 \qquad (6)$$

The orbital charge q_μ is the sum of contributions $q_{i\mu}$

$$q_\mu = \sum_i q_{i\mu} \qquad (7)$$

With eqs 5–7, the valence V_μ can be reformulated

$$V_\mu = \sum_i n_i' q_{i\mu} - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2 \qquad (8)$$

We now assume that orbitals ω_i are doubly occupied for $i = 1$ to k, i.e., $n_i' = 2$. For $i = k + 1 ... m$ orbitals, ω_i are partially occupied or unoccupied. With the additional knowledge that $\sum_{i=1}^k q_{i\mu}$ is the total charge of orbital μ minus the charge of the open shell, V_μ can be rewritten as

$$V_\mu = 2 \sum_i^k q_{i\mu} + \sum_{i=k+1}^m n_i' q_{i\mu} - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2$$

$$= 2(q_\mu - \sum_{i=k+1}^m q_{i\mu}) + \sum_{i=k+1}^m n_i' q_{i\mu} - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2$$

$$= (2q_\mu - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2) + \sum_{i=k+1}^m (n_i' - 2) n_i' a_{i\mu}^2 \qquad (9)$$

Each term in the last sum is zero for $n_i' = 2$ or 0. Therefore, the final form of the atomic valence contribution μ is

$$V_\mu = (2q_\mu - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2) + \sum_i (n_i' - 2) n_i' q_{i\mu}^2 \qquad (10)$$

The atomic valence V_A of atom A can now be formulated as

$$V_A = \sum_\mu^A (2q_\mu - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2) + \sum_\mu^A \sum_i (n_i' - 2) n_i' a_{i\mu}^2 \qquad (11)$$

We had previously defined a standard valence for each atom[5] (e.g., $V_B^0 = 3$, $V_C^0 = 4$, $V_N^0 = 3$, and $V_O^0 = 2$) in line with the standard rules of valence. A valence reduction is now defined as

$$\Delta V_A = V_A^0 - V_A = \Delta V_A^Q + \Delta V_A^{CI}$$

with

$$\Delta V_A^Q = V_A^0 - \sum_\mu^A (2q_\mu - q_\mu^2 - \sum_{\mu' \neq \mu} P_{\mu\mu'}^2)$$

$$\Delta V_A^{CI} = \sum_\mu^A \sum_i (n_i' - 2) n_i' a_{i\mu}^2 \qquad (12)$$

The first term is ΔV_A^Q formally obtained from closed-shell calculations. It refers to internal charge rearrangement without CI. It is therefore characteristic for zwitterions. The CI term ΔV_A^{CI} serves to characterize diradicals.

To avoid cancelation of negative and positive contributions from different atoms, the absolute values of ΔV_A^Q are added in the molecule. The second CI terms ΔV_A^{CI} are always positive and can be directly added.

A zwitterion is now defined as a species where

$$0 \ll \Delta V_M^Q \approx 2$$

with

$$\Delta V_M^Q = \sum_A^M |\Delta V_A^Q| \qquad (13)$$

and a diradical is defined as a species where

$$0 \ll \Delta V_M^{CI} \approx 2$$

with

$$\Delta V_M^{CI} = \sum_A^M \Delta V_A^{CI} \qquad (14)$$

This is based on the assumption that an ideal zwitterion is characterized by a transfer of a single electron from one atom
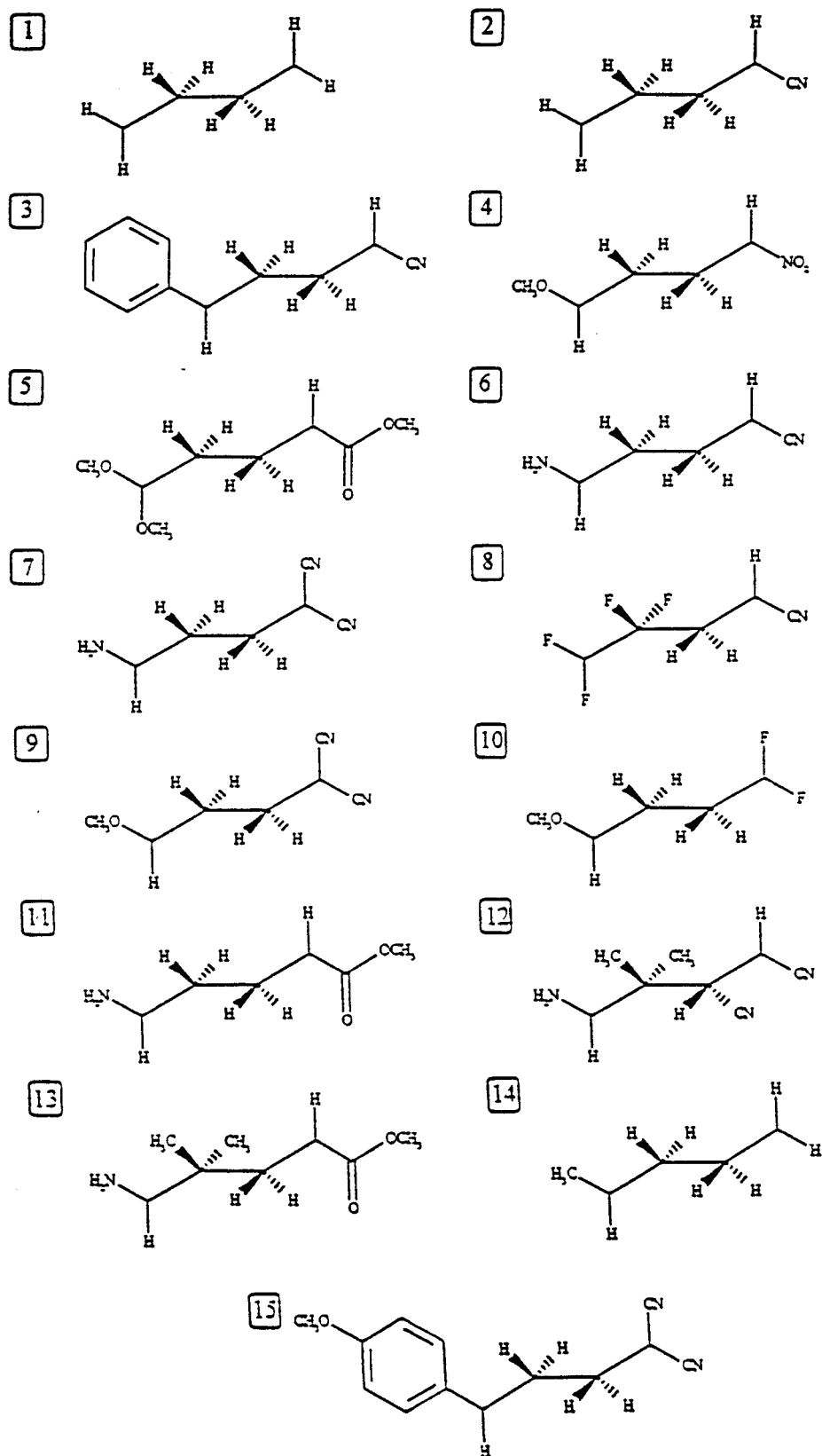
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Figure 1. Numbering of substituted tetramethylenes.

to another atom and that a diradical has two lone electrons at two radical centers. In the application, eqs 13 and 14 are used.

III. Solvation Model

In the PCM the solvent is considered as an infinitely extended, homogeneous polarizable dielectric with the dielectric constant ϵ. The solute molecule is considered to be embedded in the dielectric as a cavity. The dielectric is polarized by the electric field of the solute molecule. In turn, the dielectric induces a field in the cavity, which has an effect on the solute molecule. This induced field is called the reaction field. It can be described as a perturbation V_R of the Hamiltonian $H^{(0)}$. The

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TABLE 1: Diradical (D) and Zwitterion (Z) Character of Substituted Tetramethylenes in Gas Phase and Nonpolar Solvent Based on Valence Reduction ΔV and Dipole Moment μ (debye)

compound[a]	gas phase ($\epsilon = 0$)			benzene ($\epsilon = 2.28$)			D/Z	
	ΔV_M^{CI}	ΔV_M^Q	μ	ΔV_M^{CI}	ΔV_M^Q	μ	calcd	exptl
1	1.998	0.064	0.00	1.998	0.062	0.00	D	D
2	1.998	0.158	2.55	1.997	0.215	3.38	D	D
3	1.996	0.334	2.44	1.996	0.371	3.03	D	D
4	0.000	3.581	21.46	0.000	3.532	24.06	Z	Z
5	0.000	2.674	20.28	0.000	2.616	21.53	Z	Z
6	1.994	0.543	1.96	1.989	0.640	2.81	D	Z
7	1.993	0.641	2.78	0.000	2.133	24.85	D,Z	Z
8	1.998	0.749	0.45	1.998	0.764	1.08	D	D
9	1.994	0.713	1.54	0.000	2.212	23.65	D,Z	Z
10	1.997	0.887	1.25	1.997	0.879	1.46	D	D
11	0.000	2.076	19.36	0.000	2.067	21.23	Z	Z
12	0.000	2.437	17.98	0.000	2.405	20.94	Z	Z
13	0.000	2.267	18.68	0.000	2.204	20.16	Z	Z
14	1.998	0.092	0.18	1.998	0.085	0.07	D	D
15	1.999	0.768	3.03	1.998	0.932	6.76	D	D

[a] See Figure 1.

TABLE 2: Diradical (D) and Zwitterion (Z) Character of Substituted Tetramethylenes in Polar Solvents Based on Valence Reduction ΔV and Dipole Moment μ (debye)

compound[a]	methanol ($\epsilon = 32.5$)			water ($\epsilon = 78.5$)			D/Z	
	ΔV_M^{CI}	ΔV_M^Q	μ	ΔV_M^{CI}	ΔV_M^Q	μ	calcd	exptl
1	1.998	0.062	0.01	1.998	0.062	0.01	D	D
2	1.994	0.420	4.41	1.994	0.437	4.49	D	D
3	1.996	0.478	3.99	1.998	0.486	4.06	D	D
4	0.000	3.461	27.84	0.000	3.473	28.46	Z	Z
5	0.000	2.574	23.02	0.000	2.573	23.10	Z	Z
6	0.000	2.085	24.05	0.000	2.057	23.92	Z	Z
7	0.000	2.229	30.22	0.000	2.231	30.08	Z	Z
8	1.993	0.867	1.95	1.993	0.840	1.99	D	D
9	0.000	2.274	27.00	0.000	2.359	29.04	Z	Z
10	1.997	0.884	1.63	1.994	0.857	1.65	D	D
11	0.000	2.024	22.87	0.000	2.004	23.58	Z	Z
12	0.000	2.488	24.68	0.000	2.490	24.87	Z	Z
13	0.000	2.129	22.41	0.000	2.118	22.34	Z	Z
14	1.998	0.082	0.26	1.994	0.074	0.30	D	D
15	0.000	2.740	29.52	0.000	2.756	30.02	Z	Z

[a] See Figure 1.

equation to be solved is then

$$(H^{(0)} + V_R)\psi = E\psi \quad (15)$$

In the PCM, the reaction field is described by a virtual surface charge distribution $\sigma(\mathbf{s})$ on the cavity surface S,

$$V_R(\mathbf{r}) = \int_S \frac{\sigma(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|} d\mathbf{s} \quad (16)$$

For numerical calculations the surface S is subdivided in segments i and each segment is assigned a charge q_i,

$$V_R(\mathbf{r}) = \sum_{i=1}^m \frac{\sigma(\mathbf{s}_i)S_i}{|\mathbf{r} - \mathbf{s}_i|} = \sum_{i=1}^m \frac{q_i}{|\mathbf{r} - \mathbf{s}_i|} \quad (17)$$

The total number of segments is m. The charge distribution $\sigma(\mathbf{s}_i)$ is calculated via the solution of the Laplace equation,[10]

$$\sigma(\mathbf{s}_i) = -\frac{\epsilon - 1}{4\pi\epsilon}\left(\frac{\partial V_T(\mathbf{s}_i)}{\partial n_i}\right) \quad (18)$$

ϵ is the dielectric constant of the solvent. V_T is the total electrostatic potential of the solute molecule. It consists of the

electrostatic potential V_M of the molecule without field and the potential V_R generated from the surface charge. One has to go through an iterative process to adjust the surface charge self-consistently. This procedure is implemented in SINDO1.[15] The molecular electrostatic potential (MESP) is approximated by an asymptotic density model (ADM).[24] The details of the implementation of the ADM can be found elsewhere.[25]

IV. Tetramethylenes

Tetramethylenes are formally ring opening products of cyclobutanes. In these compounds one bond is broken and they can be described as diradicals or zwitterions. The unsubstituted *tetra*-methylene is a diradical, whereas strong donor or acceptor substituents can stabilize zwitterions. A comprehensive review of the properties of unsubstituted tetramethylenes as well as a model for stereochemical dynamics based on ab initio 6-31G* plus CI calculations has been recently given by Doubleday.[26] Since tetramethylenes exist only as intermediates in a reaction, their direct investigation is experimentally difficult. Zwitterionic intermediates can be detected with alcohols via their products.[27] A better approach for an experimental distinction is the investigation of polymerization reactions.[7] Homopolymerization and cyclobutanes indicate zwitterions, alternating copolymers should be generated from diradical intermediates. Hall has investigated a large number of substituted tetramethylenes and classified them according to their character.[7] Since the experiments are done in solution, calculations of single molecules in the gas phase are not directly comparable. We had shown in the case of 1-methoxy-4,4-dicyanotetramethylene that initial discrepancies[8] can be resolved when the solvent is taken into account.[9] In a study on the influence of the solvent on the nature of a diradical tetramethylene intermediate, Padias and Hall[27] showed that for the spontaneous thermal reactions of *p*-methoxystyrene and methyl-3,3-dicyanoacrylate several reaction products are observed: a 1/1 alternating copolymer, a double Diels−Alder adduct, and the cyclobutane adduct. In dipolar aprotic solvents, no polymerization occurs and the double Diels−Alder adduct is favored, while in protic polar solvents cyclobutane formation competes with copolymerization. In nonpolar solvents, copolymerization dominates. This seems to cover the range from zwitterions to polar diradicals to nonpolar diradicals. Huisgen[27] argued that the nature of the donor and acceptor substituents determines the nature of the tetramethylenes also in solution. A polar solvent would only enhance the rate of reaction, but would not change it from diradical to zwitterionic. Influenced by Huisgen, Padias and Hall[28] excluded a switch from diradicals to zwitterionic tetramethylenes even in polar solvents. The main factors influencing the products in solution are the solvent polarity and the ability of the solvent to interact with diradical tetramethylene. A survey on zwitterion and diradical tetramethylenes as initiators of charge-transfer polymerizations gives a detailed account of this development.[29] More recently the aspect of trapping the diradical intermediate has received new emphasis.[30] There is related work on β-lactones[31] which discusses the formation of zwitterion intermediates in terms of solvent effects.

In the following, we want to demonstrate that the nature of the solvent can influence the character of the tetramethylene and that, in particular, it can switch the character from diradical to zwitterionic. For this purpose we have studied 15 different tetramethylenes in their trans-form (Figure 1) with SINDO1. This form has the appropriate structure for polymerization.[7] The *trans*-tetramethylene diradicals can be expected to be precursors for copolymers, whereas the zwitterions can be precursors of

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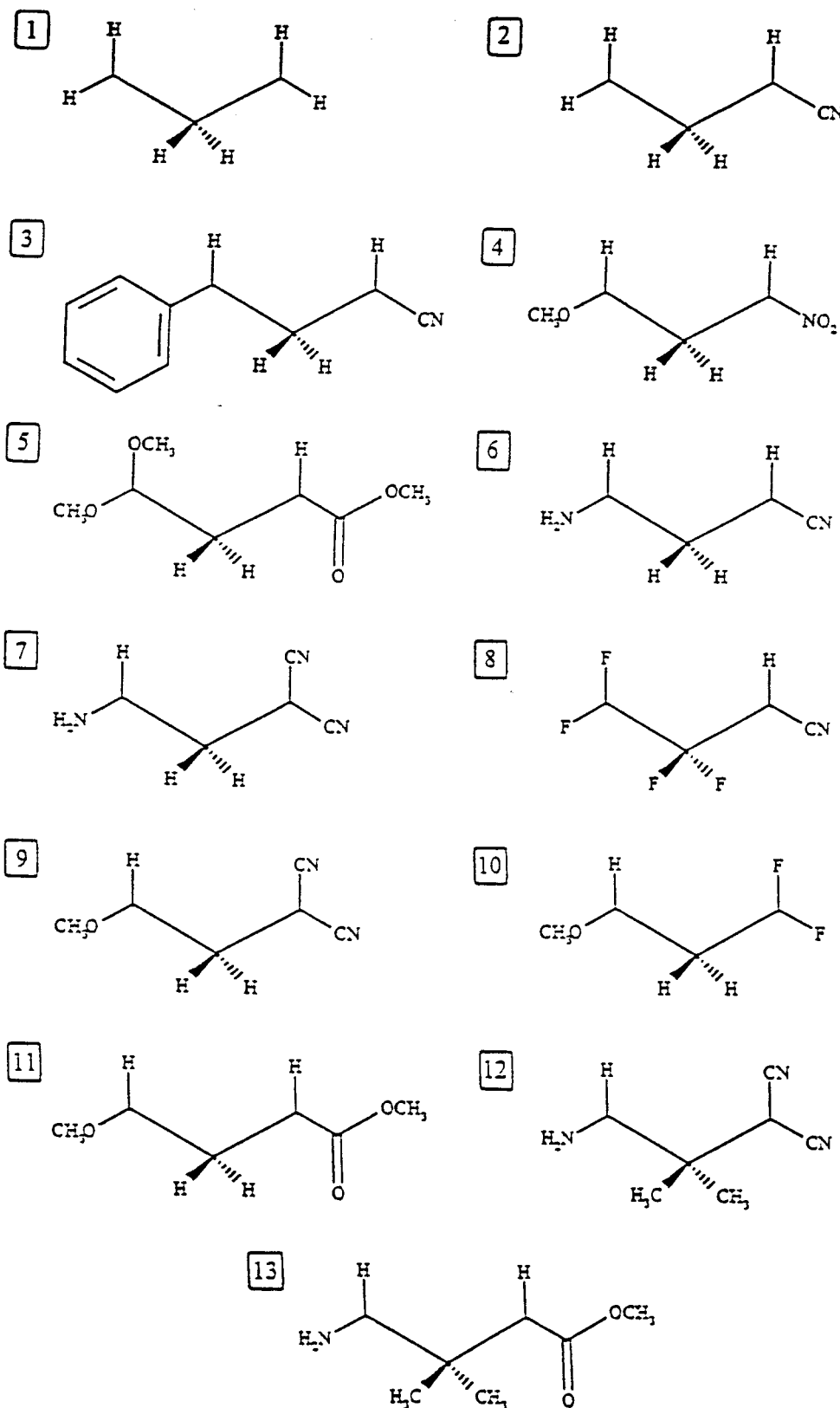*J. Phys. Chem. B, Vol. 102, No. 34, 1998* **6609**

Figure 2. Numbering of substituted trimethylenes.

homopolymers. The gauche form is not considered here, because it does not provide essentially new aspects for the following considerations, and it would be more important for cyclization. Compounds **9** and **15** are the repeatedly mentioned 1-methoxy-4,4-dicyanotetramethylene and the tetramethylene formed from combined *p*-methoxystyrene and methyl-3,3-dicyanoacrylate, respectively. We have repeatedly demonstrated

that SINDO1 is capable of describing thermal and photochemical reaction mechanism on the CI level.[12−14] In the present case the key question is the nature of ground state. For this purpose, a 4 × 4 CI is sufficient with single and double excitations from HOMO to LUMO.[1] We have optimized the geometries of *trans*-tetramethylenes on this CI surface. The solvent was introduced as a perturbation as described in the

previous section. We have chosen four different situations: gas phase ($\epsilon = 0$); solvent, benzene ($\epsilon = 2.28$); solvent, methanol ($\epsilon = 32.5$); and solvent, water ($\epsilon = 78.5$). They are representative of situations for the free molecule, almost nonpolar solvent, and polar solvent of different polarity.

The results for gas phase and nonpolar solvent are in Table 1. The classification as diradical (D) or zwitterion (Z) is based on the contributions derived in eqs 13 and 14. A diradical has a high ΔV_M^{CI} value and a low V_M^Q value, whereas for a zwitterion the situation is reversed. Besides, the magnitude of the calculated dipole moment provides a good indication. Diradicals have dipole moments of less than 5 D, whereas zwitterions have dipole moments of more than 15 D. We observe a switch from diradical to zwitterion for compounds **7** and **9** as a result of the solvent. This means that the transition from gas phase to solvent is particularly crucial for these two compounds. If the polarity of the solvent is increased, other diradicals are also converted to zwitterions. This can be seen from Table 2. Here the compound **15** is the prominent case. But also compound **6** switches its character. It is clear that zwitterions in the gas phase do not change character in solution, because the zwitterionic character can only be enhanced by increased polar character of the solvent. This table shows no perfect agreement between experimental and theoretical results. There remains still quite a number of diradicals whose character is found unchanged even in water.

V. Trimethylenes

Trimethylenes can be considered as ring opening products of cyclopropanes. Recent ab initio calculations studied the potential surface for stereo mutation[32,33] and isomerization to propene.[34] Much earlier Cram and co-workers[35−38] discussed the importance of zwitterions and diradicals as intermediates of ring opening reactions of substituted cyclopropanes. This influence of the solvent polarity on the activation and rate constant was measured for epimerization reactions.[37,38] Zwitterionic transition states were deduced from a large solvent polarity dependence on the rate. In contrast, an absence of isomerization rate dependence on solvent polarity was considered as indication for a diradical transition state. No polymerization reactions were studied in this case. To study the ring opening with respect to diradicals and zwitterions, we selected 13 trimethylenes which are presented in Figure 2. Again these trimethylenes are optimized on a 4×4 CI surface with SINDO1 for the gas phase and for the solvents benzene, methanol, and water. The results for the gas phase and benzene are in Table 3. The labeling corresponds to the one for the tetramethylenes. This means the substituents for compounds with the same number in Figures 1 and 2 are the same. It is gratifying to see that there is a close analogy between trimethylenes and tetramethylenes. Except for trimethylene, compound **7**, which appears as a zwitterion already in the gas phase, though it is found to be a diradical as tetramethylene, the analogy is striking. This means the donor−acceptor properties of the substituents are the key features to determine the nature of the ground state, and to a lesser extent, it is the frame. The classification is here again unique both from ΔV_M^{CI}, ΔV_M^Q, and μ values. Only in the case of trimethylene compound **9** a switch from diradical to zwitterion is observed.

If the polarity of the solvent is greatly increased, a switch of trimethylene compound **6** from diradical to zwitterion is predicted. The corresponding tetramethylene changes its character in the same way. It is striking that the behavior of trimethylenes and tetramethylenes from Tables 2 and 4 is identical.

TABLE 3: Diradical (D) and Zwitterion (Z) Character of Substituted Trimethylenes in Gas Phase and Nonpolar Solvent Based on Valence Reduction ΔV and Dipole Moment μ (debye)

compound[a]	gas phase ($\epsilon = 0$)			benzene ($\epsilon = 2.28$)			D/Z
	ΔV_M^{CI}	ΔV_M^Q	μ	ΔV_M^{CI}	ΔV_M^Q	μ	
1	1.943	0.077	0.34	1.942	0.075	0.38	D
2	1.946	0.162	2.29	1.932	0.212	2.87	D
3	1.939	0.312	2.29	1.937	0.337	2.79	D
4	0.001	3.467	16.70	0.000	3.462	19.10	Z
5	0.000	2.598	14.05	0.000	2.575	14.98	Z
6	1.917	0.505	2.20	1.817	0.559	3.16	D
7	0.001	2.036	15.91	0.000	2.084	19.31	Z
8	1.949	0.710	1.88	1.911	0.748	2.12	D
9	1.894	0.673	2.69	0.000	2.165	19.28	D,Z
10	1.993	0.909	2.58	1.992	0.891	2.98	D
11	0.001	1.972	13.45	0.000	1.994	14.86	Z
12	0.000	2.170	12.73	0.000	2.199	15.56	Z
13	0.000	2.190	13.13	0.000	2.177	14.40	Z

[a] See Figure 2.

TABLE 4: Diradical (D) and Zwitterion (Z) Character of Substituted Trimethylenes in Polar Solvents Based on Valence Reduction ΔV and Dipole Moment μ (debye)

| compound[a]	methanol ($\epsilon = 32.5$)			water ($\epsilon = 78.5$)			D/Z
	ΔV_M^{CI}	ΔV_M^Q	μ	ΔV_M^{CI}	ΔV_M^Q	μ	
1	1.942	0.074	0.45	1.942	0.094	0.45	D
2	1.868	0.367	4.14	1.861	0.379	4.23	D
3	1.928	0.419	3.37	1.927	0.425	3.41	D
4	0.000	3.433	22.63	0.000	3.442	21.08	Z
5	0.000	2.558	16.36	0.000	2.554	16.60	Z
6	0.000	2.050	21.70	0.000	2.042	21.76	Z
7	0.000	2.247	24.74	0.000	2.351	26.34	Z
8	1.867	0.865	2.55	1.483	0.886	2.96	D
9	0.000	2.318	24.60	0.000	2.335	24.74	Z
10	1.992	0.894	3.39	1.983	0.857	3.37	D
11	0.000	1.986	16.49	0.000	1.990	16.71	Z
12	0.000	2.384	19.32	0.000	2.429	20.01	Z
13	0.000	2.130	16.17	0.000	2.186	16.26	Z

[a] See Figure 2.

VI. Relative Stability of Diradicals and Zwitterions

We were interested to study the conversion from diradical to zwitterion with increasing dielectric constant ϵ in more detail. For this purpose we chose tetramethylene compound **6** (i.e., 1-amino-4-cyanotetramethylene). We found in benzene two structures. Besides the lower minimum which was a diradical, there was a higher lying zwitterionic structure. The two structures were distinctly different in their CC tetramethylene bond lengths. The zwitterion has a longer bond length for the central bond and the bond adjacent to the CN group. In methanol, only a diradical structure was found. It is therefore conceivable that the increase of solvent polarity switches the stability from diradical to zwitterion continuously so that the diradical is eventually lost. Such a behavior is illustrated in Figure 3. This demonstrates the importance of geometry optimization in solution. After completion of this work, a paper on geometry optimization in the PCM[39] appeared which underlines this point. Of course, without the solvent, the polarity of the tetramethylenes is governed by the strength of donor and acceptor groups. In this sense a zwitterion may appear already without the solvent. A similar question was recently addressed by Sustmann and Sicking[40] for the Diels−Alder reaction which forms hexamethylene intermediates.

VII. Conclusion

We have demonstrated that a valence criterion previously introduced is a useful tool for the classification of diradicals

Tetramethylenes and Trimethylenes

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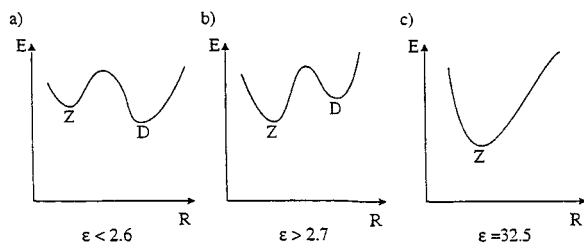
Figure 3. Potential curve scheme in dependence of the dielectric constant ϵ: (a) two minima, diradical (D) more stable than zwitterion (Z); (b) two minima, zwitterion (Z) more stable than diradical (D); (c) one minimum, zwitterion (Z).

and zwitterion in the gas phase and in solution. SINDO1 calculations in the gas phase and different solvents for tetramethylenes showed perfect agreement with the classification from experiment. The analysis demonstrated that the solvent can be responsible for a switch from diradical to zwitterionic character for borderline cases, whereas other typical diradicals will not switch their character even in highly polar solvents. Trimethylenes show a completely analogous behavior as tetramethylenes for the same substituents.

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