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Importance of Dipolar Resonance Structures in Determining Ground State Charge Distribution

Alan R. Katritzky* and Mati Karelson[a]
Department of Chemistry, University of Florida,
Gainesville, Florida 32611-2046, U.S.A..

Abstract: AM1 SCRF calculations indicate the substantial importance of solvent-assisted polar resonance in acrolein and vinylamine.

Recently,[1] it was claimed on the basis of *ab initio* molecular orbital calculations using the 6-31G* basis set and Bader's electronic charge localization method,[2,3] that polar resonance forms are unimportant in acrolein **1** and vinylamine **2** and that the electron distribution in both is strikingly similar to that in 1,3-butadiene **3**. This result is a serious challenge for organic chemists who have employed the resonance concept over many decades. The calculations mentioned above refer to the molecules in the gas phase at low pressure where intermolecular interactions are absent. This corresponds to the situation in interstellar space. However, the vast majority of organic reactions have been studied in condensed media. Recently we showed using semiempirical self-consistent reaction field (SCRF) calculations that polarizable media can have decisively large effects on the charge distributions, stabilization energies and geometries of conjugated systems (radical and ionic carbon centers,[4,5] aromatic heterocycles[6,7] and disubstituted ethylenes[8]). It was therefore of great importance to study the interplay of polar resonance effects with solvent reaction field for the three above-mentioned molecules (**1-3**).

We again used the LCAO MO SCRF method[5-10] with Dewar's AM1[11,12] semiempirical parametrization. The essence of the SCRF method can be summarized as the use of molecular Hamiltonians in the Hartree-Fock equations, perturbed by the reaction field from the polarizable medium. The reaction field is found iteratively until self-consistency is reached of the intramolecular electronic field (cf. Ref. 9,10). The solute molecule is assumed to be embedded into a cavity in the polar medium of uniform dielectric constant. The geometric form of the cavity has been widely discussed in the literature (cf. Ref. 13-18) but our experience has shown that, for comparatively rigid molecules without long side-chains, a simple spherical cavity is a satisfactory approximation. In the present work we assumed for the solute molecules spherical cavities of radius $a_0 = 2.5$ Å.

The AM1 calculated energies and geometries of molecules **1-3** in the gas phase (relative dielectric permittivity $\varepsilon = 1$) and aqueous solution ($\varepsilon = 80$), are given in Tables 1 and 2. The calculations were carried out for molecules **1** and **3**, with the two double bonds *cis*-, and *trans*- and at 90° to each other.

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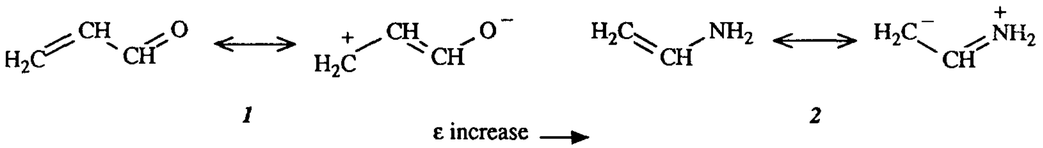
[a] Permanent address: Laboratory of Chemical Kinetics and Catalysis, Tartu University, Tartu, 202400, Estonia

The calculated bond lengths and bond angles of all three molecules are rather insensitive to medium effects (cf. Table 2.), substantially less than for polar heterocyclic compounds[6,7]. However, there is significant solvent-assisted change in the dipole moments of molecules **1**-**3** due to charge redistribution in their π-electron system (cf. also Fig. 1.) corresponding to the increase in the weight of the more polar resonance form of the compound, e.g.



1

2

In Ref. 1, the similarity of the barriers to rotation at the single carbon-carbon bonds in acrolein and butadiene was emphasized. The 6-31G* calculated barrier heights (8.2 kcal/mol for **1** and 5.85 kcal/mol for **3**), much higher than ethane (2.75 kcal/mol) or ethanol (1.29 kcal/mol),[19] indicate substantial π-orbital overlap at the central C-C bond in molecules **1** and **3**. The AM1 calculations for the isolated molecules give much smaller rotational barriers (cf. Table 1.), but for acrolein the barrier increases significantly in polar medium, whereas there is no medium effect on the 1,3-butadiene molecule, confirming the solvent assistance of polar resonance.

The Mulliken charge distributions obtained in the present calculations (cf. Fig. 1) show relative partial charges on the vinyl carbon atoms, in agreement with the resonance concept, which increase with the medium dielectric permittivity. Consequently, the polar resonance forms are of substantial importance in compounds **1** and **2**, especially when solvent assistance is present.

Table 1: AM1 Calculated Heats of Formation and Dipole Moments of Acrolein, Vinylamine and 1,3-Butadiene for the Isolated Molecules and for Aqueous Solution.

Molecule	**Conformation**	**ΔH_f (kcal/mol)**		**Dipole Moment (D)**	
		$\varepsilon = 1$	**$\varepsilon = 80$**	**$\varepsilon = 1$**	**$\varepsilon = 80$**
Acrolein	*cis*	-16.30	-20.14	2.534	3.054
	trans	-16.51	-23.43	3.065	4.224
	90°	-14.73	-18.63	2.615	3.177
Vinylamine	opt[1]	11.67	10.53	1.505	1.703
Butadiene	*cis*	30.69	30.69	0.041	0.052
	trans	29.91	29.91	0.000	0.000
	90°	31.90	31.90	0.024	0.031

[1] Optimum geometry.

Table 2: AM1 Calculated Bond Lengths and Bond Angles in Acrolein **1**, Vinylamine **2** and 1,3-Butadiene **3** (optimum geometry) in Two Different Media. Geometric Parameters are Defined in Figure 1.

		(a) Bond Lengths.							**(b) Bond Angles.**					
Comp	**ε**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**ab**	**bc**	**bd**	**ae**	**af**	**bg**
1	1	1.332	1.468	1.234	1.114	1.100	1.098	1.102	123.2	124.0	115.0	122.0	122.4	121.7
	80	1.335	1.468	1.237	1.112	1.102	1.102	1.100	123.1	123.0	116.0	123.1	122.5	120.5
2	1	1.344	1.392	0.995	0.996	1.095	1.095	1.108	126.2	114.1	115.1	123.6	120.8	120.5
	80	1.345	1.390	0.996	0.997	1.095	1.094	1.108	125.4	114.1	115.7	123.5	120.6	121.3
3	1[1]	1.335	1.449	1.098	1.098	1.105	—	—	123.5	—	—	120.7	122.0[2]	—

[1] The calculated geometric parameters for 1,3-butadiene are virtually the same in the two media.

[2] Angle between bonds a and c.

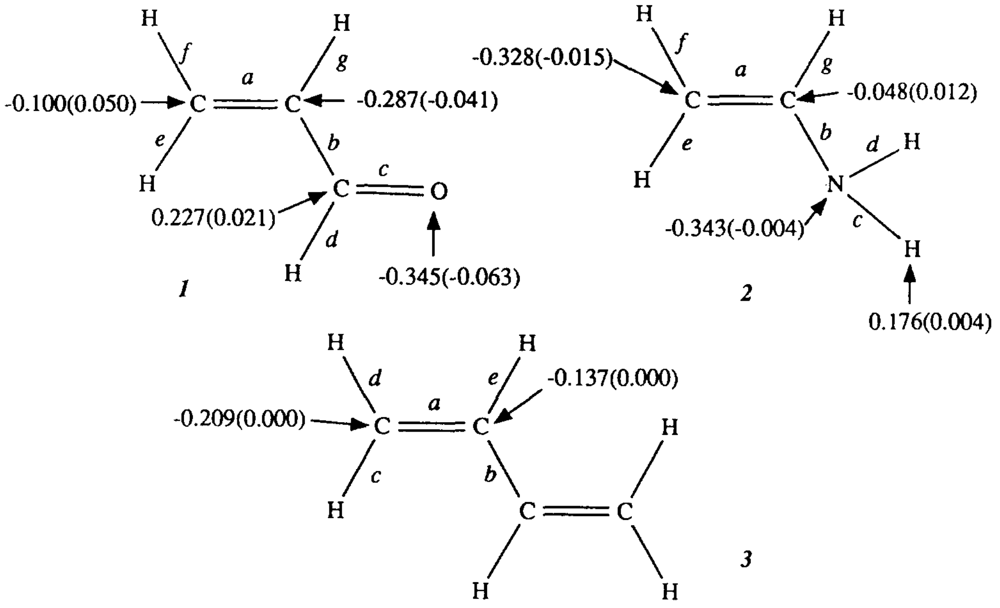


Figure 1: The AM1 Calculated Mulliken Partial Charges in Acrolein, Vinylamine and Butadiene. Charge Shifts Due to the Embedding of Molecules into Dielectric Medium with ε = 80 are given in Parentheses.

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