Tetrahedron Letters,Vol.30,No.44,pp 5981-5984,1989
Printed in Great Britain

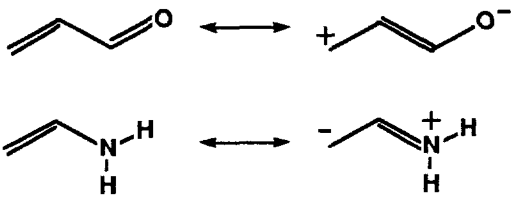
0040-4039/89 $3.00 + .00
Pergamon Press plc

CHARGE DENSITY DISTRIBUTION IN ACROLEIN, BUTADIENE AND VINYLAMINE UNIMPORTANCE OF DIPOLAR RESONANCE STRUCTURES IN DETERMINING THE GROUND STATE CHARGE DISTRIBUTION

Kenneth B. Wiberg and Robert E. Rosenberg
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Abstract: The charge distributions in acrolein, butadiene and vinylamine have been calculated from 6-31G** wave functions. A comparison of the distributions at the vinyl group for the planar and 90° rotated forms indicated no significant charge shift. A comparison between butadiene and the other compounds again indicated no significant differences. It is concluded that the dipolar structures do not contribute significantly to the ground state structures, but rather they might best be considered as indicators of the easiest mode of charge polarization in the presence of an attacking reagent.

α,β-Unsaturated carbonyl compounds and enamines have received extensive synthetic utilization because of their high reactivity. The reactivity has generally been ascribed to changes in charge distribution arising from the dipolar resonance structures:[1]



However, it is well recognized that the contribution of any canonical structure is related to its energy. The larger the energy difference between two canonical structures, the smaller the contribution of the higher energy structure. In the above cases, the dipolar structures will have much higher energies than the normal structures because they involve extensive charge separation, and because in the case of acrolein it has one less bond than the other structure. These considerations have led us to examine the charge distributions in these molecules. For comparison, we also have examined butadiene, a compound where the charge separation would be expected to be minimal.

The question could be studied in either one of two ways. First, the resonance interaction would be eliminated by rotating one half of each conjugated system by 90°. If the dipolar structures were important for the planar molecules, one should see a large charge shift on rotation. Second, one might study the molecules using an average geometry for the vinyl groups, calculating the charge density distribution for each, and then comparing the distributions with that of butadiene. We have employed both of these procedures giving the results presented below.

The relative energies of several rotamers of acrolein are shown in Figure 1.[2] The rotated form is significantly higher in energy than the equilibrium structure, and the calculated barrier is somewhat larger than that for butadiene (5.85 kcal/mol). Since the 90° form is not positioned to incorporate the dipolar resonance forms, but the equilibrium structure is, chemists have cause to think that the dipolar structures are important.

The problem of assigning electron populations to atoms in molecules has been of interest to chemists for a long time, but only recently has a rigorous method for partitioning the charge in molecules been developed by Bader and coworkers.[3] The charge density (ρ) may be obtained from the mo wave functions. Between each pair of bonded atoms there is a point of minimum charge density along the bond, but a maximum in ρ in other directions. It is known as the bond critical point. Starting at this point, one develops rays for which the charge density decreases most rapidly, and the set of such rays taken in all directions from the critical point forms a surface which separates the atoms in a *quantum mechanically rigorous fashion*. The set of surfaces separates the molecules into atomic subregions. Integration of the charge density within such a region gives the electronic population on that atom. The dipolar resonance structures for acrolein, if important, would result in population shifts. The results of the numerical integration of the charge density within the atomic boundaries also are shown in Figure 1.

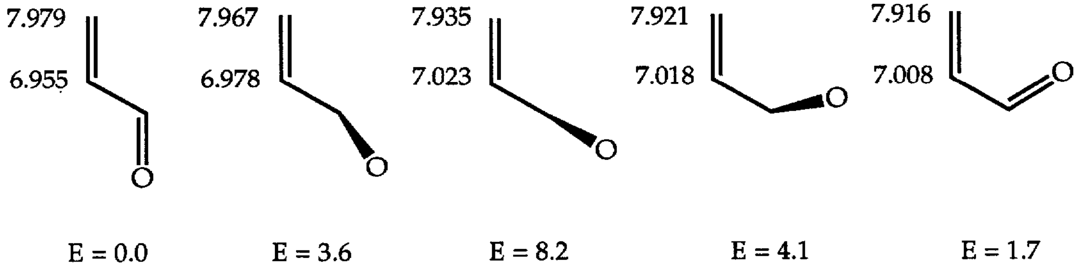


Figure 1. Electron populations derived from 6-31G** wave functions for the groups in planar and rotated acrolein. The relative calculated energies are given in kcal/mol.

Butadiene is expected to have the least zwitterionic character of the three molecules. The terminal CH_2 has 8.007 electrons which is close to the expected 6+1+1 = 8.000 e, while the middle CH has 6.991 e as compared to the expected 6+1 = 7.000 e. These populations do not change significantly upon rotation to 0° or 90° forms, even though the energy differences are substantial. The electron populations at the vinyl group of trans acrolein are nearly identical to those in butadiene. The dipolar resonance model would predict charge depletion at the terminal carbon of the planar form, and this is not observed. Moreover, upon rotation, the populations change relatively little, and the change is continuous from 0° to 180°. The small change in population on rotation corresponds to a coulombic interaction between the carbonyl group and the double bond in cis-acrolein. The large C=O bond dipole will cause a charge shift in the C=C group of the cis form leading to an induced dipole with the opposite sense to the C=O dipole. In this way, the electron population at the terminal methylene group of the cis form will be reduced. In vinylamine, the terminal CH_2 group has 7.936e, which is slightly smaller than found for butadiene. If the dipolar resonance structure contributed significantly to the ground state charge distribution, the population in vinylamine should have been greater than that for butadiene.

The π-electron populations within each of the atomic regions also are of some interest. The populations for the terminal CH_2 and the adjacent CH groups of trans-acrolein are 0.885 and 0.962 e respectively. With the cis form, the corresponding populations are 0.844 and 1.003 e. The shift in the π-population at the terminal carbon (0.041 e) is a major part of the shift in the total charge (0.063 e). This should be expected since the magnitude of the induced dipole depends on the polarizability, and the π-electrons are more polarizable than the σ-electrons. The depleted π-population at the CH_2 group could be due either to a polarization of the π-bond by the electron deficient carbon of the carbonyl group, or to some contribution from the dipolar resonance form. In either case, the shift is compensated in the σ-system leading to little net change from that found in butadiene. The π-populations for the 90° rotated form are not well defined since σ-π mixing occurs. For the highest occupied mo, which corresponds largely to the π-component of the terminal double bond, the π-populations at the CH_2 and CH groups are 0.965 and 0.938 e respectively. The significance of these values remains to be determined.

A related and more conventional method to examine charge distribution is to integrate the electrons above the π nodal plane and project this density into that plane.[4] Figure 2 illustrates the projection density. Each contour represents a given value of the charge density. As contours go in toward the atoms, the value for successive contours doubles. As can be seen, the three structures look remarkably similar in the olefinic region. One also can see the large polarization effected by the heteroatom in its bond to carbon compared to the olefinic bond in butadiene.

Dipolar resonance contributors would show up as charge depletion in the terminal carbon of acrolein, and charge accumulation on the terminal carbon in enamine. By comparing these termini to that in butadiene, one can see that there is almost no contribution by these dipolar resonance structures.

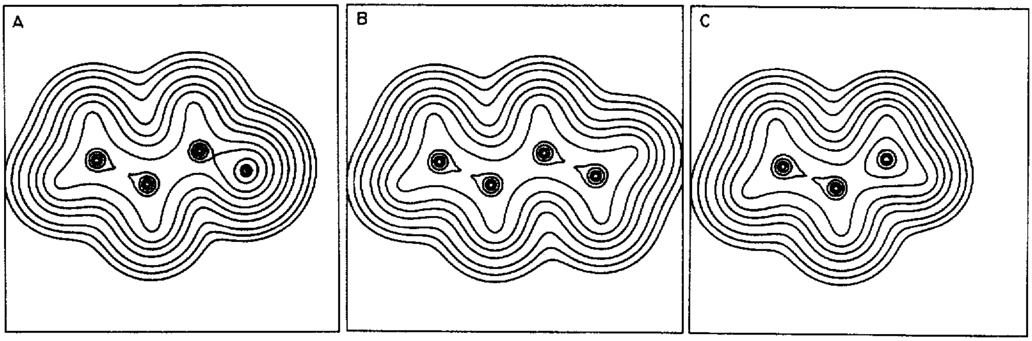


Figure 2. Projection density plots for a. acrolein, b. butadiene and c. vinylamine.

Although the dipolar resonance structures do not contribute significantly to the charge distribution in the ground states of these molecules, they do correctly indicate the type of reactivity to be expected. Therefore, the dipolar structures might best be thought of as predictors of the direction in which charge is more easily polarized in the presence of an attacking reagent. The same is probably true for the dipolar resonance structures for substituted aromatic compounds. They also indicate the nature of the changes in electron populations on going to the π-π* excited states.

The Gaussian 86 program package[5] employing the 6-31G* basis set[6] was used for the geometry optimizations of all molecules and the 6-31G** basis set was used to obtain the wave functions used in calculating the electron populations. Frequency calculations confirmed the existence of minima where appropriate. Electron populations were calculated using Proaims.[7] Projection densities were calculated using a local program, Linteg.

Acknowledgement: This investigation was supported by a grant from the National Science Foundation. RER was supported by an NSF predoctoral fellowship.

References:

1 Cf. McMurry, J. "Organic Chemistry," Brooks/Cole, Monterey, CA, 1984, pp. 716, 869.

2 For previous calculations see: Breulet, J.; Lee, T. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 6250. Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14. Slee, T.S *J. Am. Chem. Soc.* **1986**, *108*, 606.

3 Bader, R. F. W. *Accts. Chem. Res.* **1985**, *18*, 9.

4 Streitwieser, A., Jr.; Collins, J. B.; McKelvey, J. M.; Grier, D.; Sender, J.; Toczko, A. G. *Proc. Natl. Acad. Sci.USA* **1979** *76*, 2499. Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980** , *1* , 81.

5 Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. S. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Gaussian 86 Gaussian Inc., Pittsburgh, PA 15129.

6 Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Francl, M. M.; Pietro, W .J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1983**, *77*, 3054.

7 Biegler-König, F. N. ; Bader, R. F. W.; Tang, T. H. *J . Comput. Chem.* **1982**, *3*, 317.

(Received in USA 5 May 1989; accepted 30 August 1989)