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HETEROCUMULENE MOLECULAR ORBITALS: KETENES, ISOCYANATES, SULFENES, AND SULFONYLAMINES

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As part of our general investigations of cycloaddition reactions by perturbation molecular orbital (PMO) theory,[2] we have carried out MO calculations on a number of heterocumulenes. The preliminary results of these calculations, which provide insight into the reactivity of heterocumulenes, are reported here.

The frontier MO's, energies, and total charges calculated by CNDO/2[3] are shown in Figure 1. The geometries of ketene and the parent isocyanate were assumed,[4] while modest geometry searches were performed for the parent sulfene and N-sulfonylamine. For sulfene in a planar geometry with all bond angles fixed at 120° and r_{CH} fixed at 1.08 Å, the lowest energy was found for r_{CS} = 1.61 Å and r_{SO} = 1.54 Å. A "perpendicular" geometry with the OSO plane perpendicular to the H_2CS plane gave a minimum energy for r_{CS} = 1.62 Å, and r_{SO} = 1.55 Å . This partially optimized "perpendicular" sulfene was calculated to be 35 kcal/mol higher in energy than the planar sulfene. A third geometrical variation tested involved pyramidalization of the CH_2 group. Bending the HCH plane 30° with respect to the CSO_2 plane without reoptimization of bond lengths resulted in a 13 kcal/mol destabilization with respect to the planar geometry. For planar N-sulfonylamine with fixed 120° bond angles, optimization gave r_{NH} = 1.06 Å, r_{NS} = 1.56 Å, and r_{SO} = 1.54 Å. Both ketene and isocyanate are characterized by low-lying vacant in-plane MO's with largest coefficients at the central atom. This, combined with the large positive charge at these centers makes them the site of attack by electrophiles. Similarly, both the large negative charge and largest HO coefficients on C and N, respectively make these the sites of electrophilic attack.[5]

The propensity of ketenes to undergo concerted $[{}_{\pi}2_s + {}_{\pi}2_a]$ cycloadditions[6-8] is the result of the electrophilicity of the central carbon atom of the ketene combined with simultaneous possibility of $[{}_{\pi}2_s + {}_{\pi}2_a]$ interaction between the ketene HO and ketenophile LU.[6,7] When the

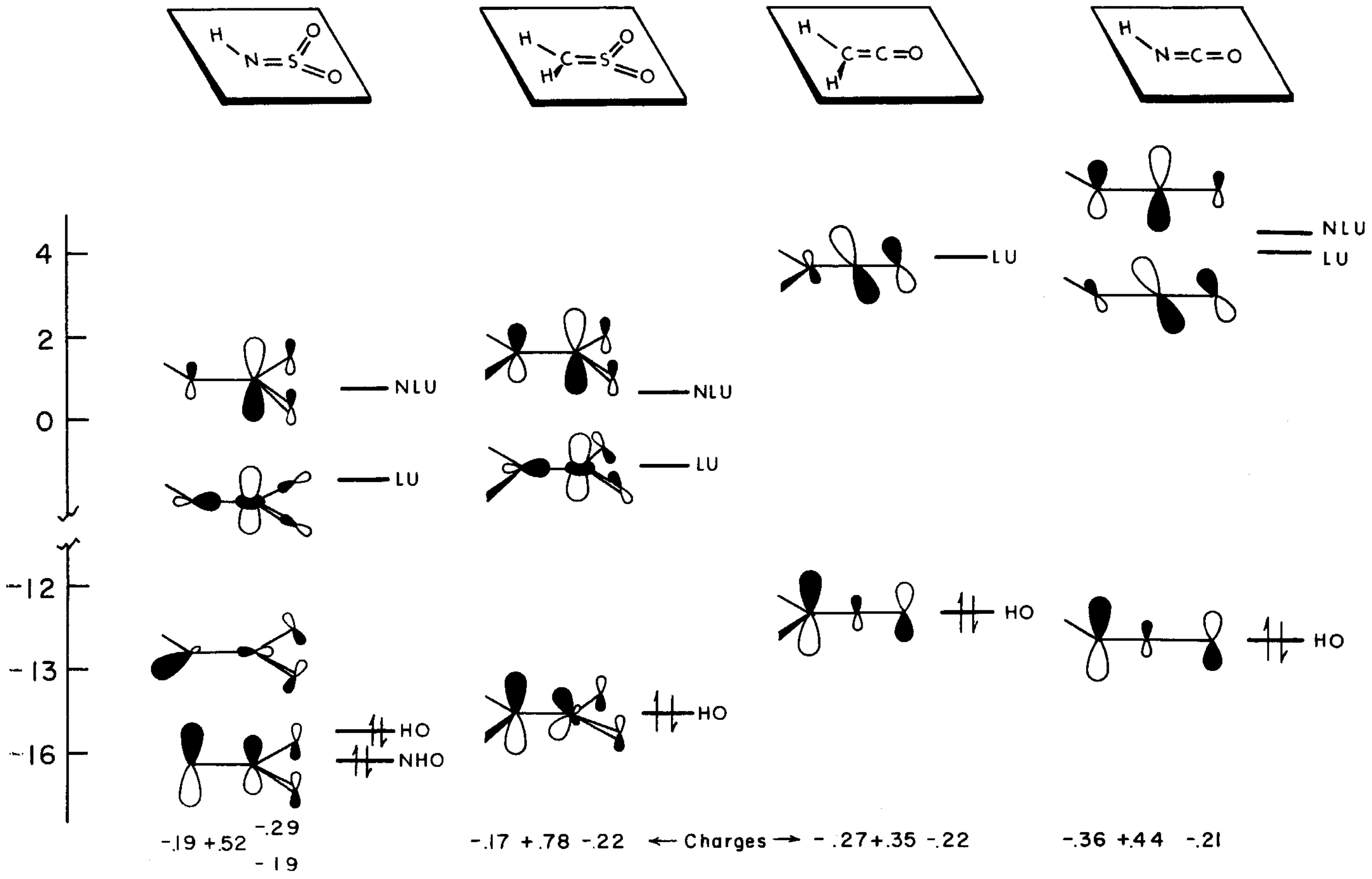

FIGURE 1. Frontier Molecular Orbital Energies and Coefficients (CNDO/2)

former interaction is enhanced at the expense of the latter by raising both the HO and LU orbital energies of the ketenophile, as with enamine-ketene pairs, a stepwise reaction involving dipolar intermediates occurs.[9] Electron-rich dienes may add in either the $[_{\pi}2_s + {}_{\pi}2_a]$ fashion, or in a $[_{\pi}4_s + {}_{\pi}2_s]$ fashion across the carbonyl group.[10]

Isocyanates are less prone than ketenes to undergo concerted reactions due to the lower energy of the isocyanate HO as compared to that of ketene.[11] Furthermore, isocyanates have a low-lying π MO, nearly degenerate with the LU, and substituents such as aryl groups should stabilize the π orbital more than the in-plane orbital. As a result only the non-concerted reactions of aryl isocyanates are expected, both because the intermediate dipolar species will be stabilized and because attack on the carbon from an out-of-plane direction cannot be accompanied by the $[_{\pi}2_s + {}_{\pi}2_a]$ interaction.

In this respect, sulfenes and the recently discovered N-sulfonylamines[12] resemble isocyanates more than they resemble ketenes. For sulfene and N-sulfonylamine the two lowest vacant orbitals are shown. The importance of d orbitals in bonding in molecules containing third-row elements is uncertain,[13] and the CNDO/2 calculations may overestimate the importance of d orbitals. However, whether or not the order of vacant orbitals is that shown, the lowest vacant orbitals of sulfenes and N-sulfonylamines are composed of orbitals heavily localized on sulfur and out-of-plane (π) at the sulfur atom. Neither sulfenes nor N-sulfonylamines should undergo concerted cycloadditions to alkenes, but sufficiently nucleophilic alkenes may add in a stepwise fashion, or electron-rich dienes may add in a concerted (4 +2) fashion.[14] With all four species, electron-deficient dienes may add in a concerted fashion if the cumulene HO-diene LU interaction becomes sufficiently great. The relative reactivities for this type of reaction should fall in the order of electrophilicities, i.e. ketene > isocyanate > sulfene > N-sulfonylamines. There is some indication of this in the literature. For example, α,β-unsaturated ketones, which have a low-lying LU orbital, undergo [4 + 2] cycloadditions to ketenes,[11] and vinylsulfenes dimerize in a [4 + 2] fashion.[15] Nitrones and nitrile oxides, which have low-lying LUMO'S,[16] undergo [4 + 2] addition to the CC, or CS double bonds of ketenes, isocyanates, and sulfenes, while diazoalkenes undergo [4 + 2] addition to the CO double bond of ketene.[17]

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1. Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972-1977.

2. K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, J. Amer. Chem. Soc. **95**, 7301 (1973) and references therein.

3. The basis set includes 3d orbitals on sulfur: QCPE 141 was used as described in detail in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, N. Y. 1970.

4. Ketene: planar, with ∠HCC=120°, ∠CCO = 180°, r_{CH}= 1.08Å, r_{CC}= 1.31Å, r_{CO}= 1.16Å, HNCO: ∠HNC = 120°, ∠NCO = 180°, r_{HN} = 0.99Å, r_{NC}= 1.32Å, r_{CO}= 1.16Å.

5. For recent reviews of and leading references to PMO treatments of reactivity, see Ref.2 and R. F. Hudson, Angew. Chemie Int. Ed. Eng., **12**, 36 (1973).

6. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic press, N. Y. 1970, p.163.

7. R. Sustmann, A. Ansmann, and F. Vahrenholt, J. Amer. Chem. Soc., **94**, 8099 (1972).

8. See, for example, K. W. Egger, J. Amer. Chem. Soc., **95**, 1745 (1973) and references therein.

9. R. Huisgen and P. Otto, ibid., **91**, 5922 (1969).

10. J. C. Martin, P. G. Gott, V. W. W. Goodlett, and R. N. Hasek, J. Org. Chem., **30**, 4175 (1965).

11. H. Ulrich, "Cycloadditions of Heterocumulenes," Academic Press, New York, 1967.

12. E. M. Burgess and W. M. Williams, J. Amer. Chem. Soc., **94**, 4386 (1972).

13. See, for example, I. H. Hillier and V. R. Saunders, Chem. Phys. Letters, **4**, 163 (1969).

14. G. Opitz, Angew.Chemie Int. Ed. Eng., **6**, 197 (1967).

15. R. Fusco, S. Rossi, S. Maiorana, and G. Pagani, Gazz. Chem. Ital., **95**, 774 (1965).

16. K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, J. Amer. Chem. Soc., **95**, 7287 (1973).

17. After submission of this work, extensive sulfene calculations were reported: J. P. Snyder, J. Org. Chem., **38**, 3965 (1973).