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THE ELECTRONIC STRUCTURE OF STABLE DELOCALIZED NITRONATE SALTS. HMO CALCULATIONS FOR DISUBSTITUTED PROPENIDES.[1]

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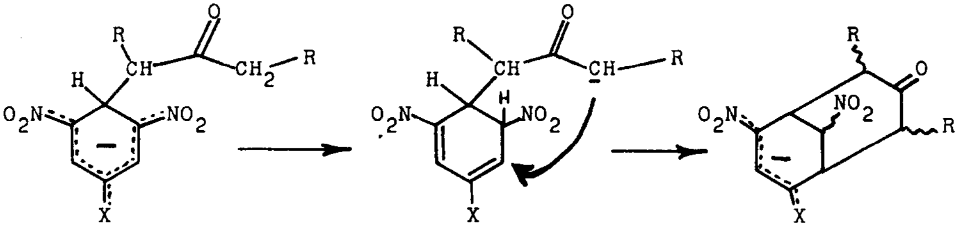
We have recently described the preparation and structural characterization of a new class of delocalized bicyclic anions of general structure 2, which arise from cyclization of appropriately structured Meisenheimer complexes.[1-5]



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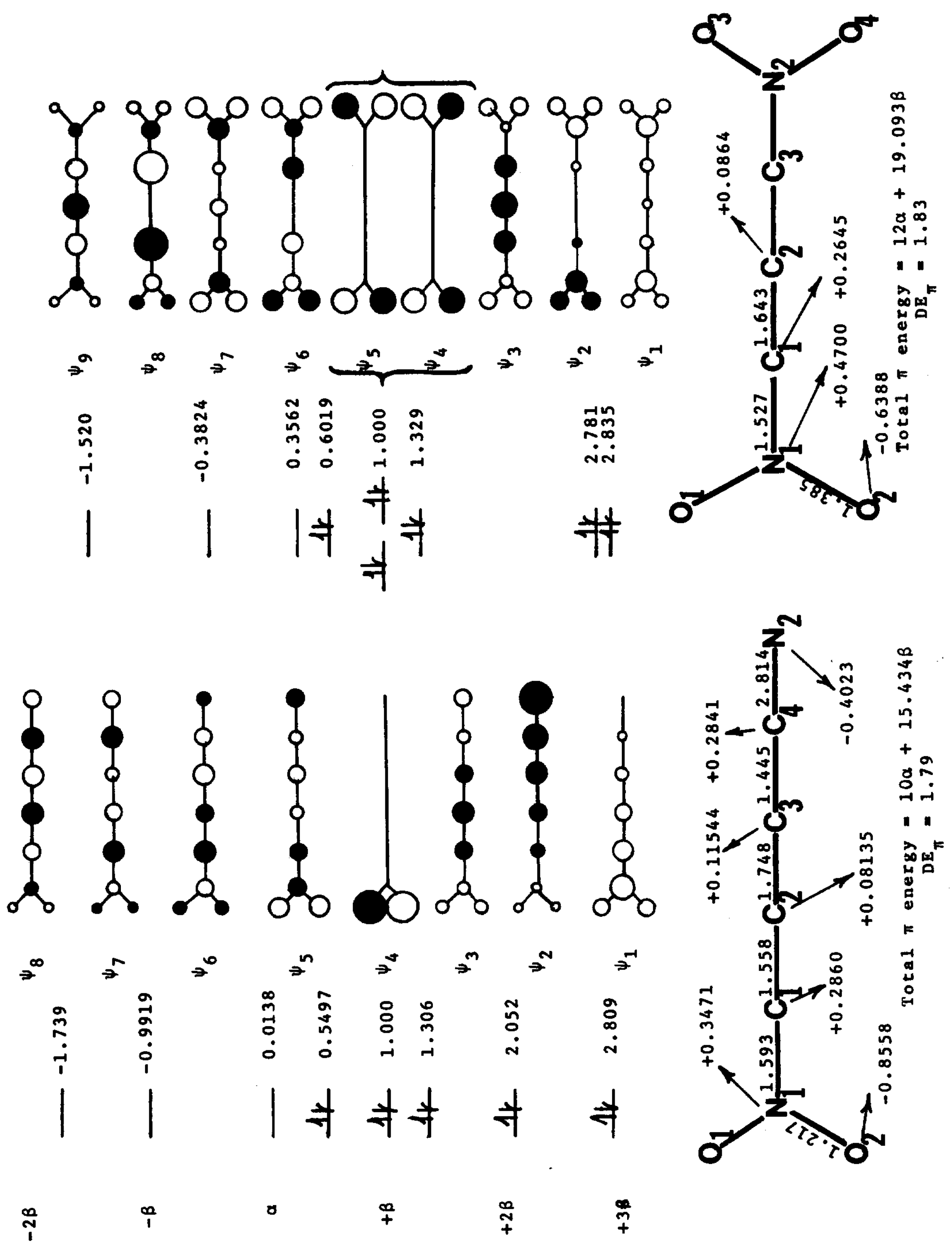
2a, X = NO_2
2b, X = CN

Formally, the anions 2 are salts of 2-cyano- or 2-nitroethene-1-nitronic acids. HMO methods have proven useful as an aid to understanding the structure and spectral properties of Meisenheimer complexes like 1,[6-9] and we report here the successful use of such methods to explain, in part, the electronic structure and properties of the delocalized portions of 2a and 2b. Qualitative orbital energy calculations for structures analogous to 2a have appeared previously,[8] but charge densities, bond orders, and the delocalization energy were not reported.

Coulomb and resonance integral values used by Heilbronner[6] were used in the calculations on structures like 1. Using $\alpha_x = \alpha_c + h_x\beta_{c-x}$ and $\beta_{c-x} = k_x\beta_{c-c}$, where h_x = 2.0 for a nitro group nitrogen, 1.0 for a cyano nitrogen and nitro oxygen, and 0.0 for all carbon atoms, and where k_x = 0.8 for C-NO_2, 0.7 for N-O, and 1.2 for C≡N, we were able to duplicate Heilbronner's calculations for 1 (X = NO_2) and other related Meisenheimer complexes.[6] The charge densities, bond orders, orbital energies, delocalization energies, and relative signs and magnitudes of the coefficients for 2a and 2b are shown in the accompanying figure. The delocalization energies, calculated relative to localized nitro, cyano, and allyl anion functions, are about the same. These data are interesting in several



Total π energy = 12α + 19.093β
DE_π = 1.83

Total π energy = 10α + 15.434β
DE_π = 1.79

respects. The energy of transition from the highest occupied to the lowest unoccupied MO is .536β in 2b and .246β in 2a. This is in qualitative agreement with the observed visible maxima of 380 and 500 nm for these anions.[1] Only one visible absorption is expected, as reported.[1] The calculated charge densities show that much of the negative charge resides on the oxygens of the nitro group and nitrogen of the cyano group, and that the carbon framework is slightly positive. Although some criticism has been directed at HMO charge density calculations in similar cyclohexadienate systems, like 1,[7] the strongly deshielded C_2-H proton in the pmr spectra of both 2a and 2b, provides support for these data. In fact, the C_2-H δ values of 8.4 and 7.4 ppm for 2a and 2b respectively,[1] parallel the calculated charge densities. This latter result is undoubtedly a fortuitous one however, as the data summarized in the accompanying figure depend on values of the coulomb and resonance integrals chosen for the heteroatoms. Using the MO coefficients and polarizabilities, we have found that slight increases in h_x and k_x (i.e., more negative coulomb and resonance integrals) result in signigicant changes in the lowest excitation energy ΔE and the charge density on C-2, q_2. For 2a, ΔE increases with increasing $k_{N-O}$and/or k_{C-N}, decreases with increasing h_N, and shows no significant change with increasing h_O. The charge density q_2, on the other hand, shows little change with increasing h_N, sharply decreases with increasing h_O and/or k_{C-N}, and increases with increasing k_{N-O}. For 2b, the charge density q_2 does not significantly change with increasing $k_{C\equiv N}$ or with increases in any parameter associated with the nitro group, but decreases moderately with increasing h_N (cyano). The excitation energy is little affected by increases in h_N (cyano) or h_N (nitro), increases sharply with h_O and k_{C-N} (nitro), and decreases sharply with k_{N-O}, and to a lesser extent with k_{C-N} (cyano).

Protonation of the anion might be expected to occur on oxygen rather than on carbon, but this has not been verified experimentally as the anions yield only polymer on acidification.[10] The conspicuous absence of the parent nitronic acids in the literature may well be a result of their tendency to polymerize.[11]

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