Ambident S_N2 Nucleophiles

Molecules that possess more than one nucleophilic site are referred to as "ambident" nucleophiles. S_N2 reactions involving these nucleophiles may lead to mixtures of products. For example, nucleophilic attack by nitrite on methyl bromide gives both nitromethane and methyl nitrite.

$$CH_3Br \xrightarrow{NO_2^-} CH_3NO_2 + CH_3ONO$$

Examine atomic charges and the electrostatic potential map for ***nitrite anion***. Which atom(s) is most electron rich? Which product would be obtained if this atom behaved as a nucleophile in its reation with methyl bromide.

Other possible ambident nucleophiles include ***cyanide anion*** (CN^-), ***methyl sulfinate anion*** ($CH_3SO_2^-$), and ***acetone enolate*** ($CH_3COCH_2^-$). Identify the most electron-rich atom(s) in each anion (based on charges alone), and indicate the major product that should result from an S_N2 reaction with methyl bromide at this atom(s).

Another way to assess nucleophilic reactivity is to examine the shape of the nucleophile's electron-donor orbital (this is the highest-occupied molecular orbital or HOMO). Examine the shape of each anion's HOMO. At which atom would an electrophile, like ***methyl bromide***, find the best orbital overlap? (Note: This would involve overlap of the the HOMO of the nucleophile and the lowest-unoccupied molecular orbital or LUMO of CH_3Br.) Draw all of the products that might result from an S_N2 reaction with CH_3Br at these atoms.

Can the ambident nucleophilicity of any of these anions be explained solely on electrostatic grounds? Solely on orbital overlap grounds? Explain your reasoning.