Systematic Studies of the *σ* and *π* Stabilizing Effects in the Nitrosyl-Containing Molecules and Their Isovalent Analogues

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Received: December 13, 2001; In Final Form: February 1, 2002

The electronic stabilization effect of the substituents on the nitrosyl-containing molecules has been studied by computing the electronic energy change (ΔE) in the isodesmic reactions, R−NO + H_2 → H−NO + RH, at the B3LYP/6-311+G(d,p) level of theory. A total of 15 substituent groups (R) which span a wide range of σ and π donating/withdrawing strength have been included. Studies were extended to three isovalent analogues, namely, the NS-, PO-, and PS-containing molecules, with the same group of substituents. Computational results show that σ-withdrawing groups strongly destabilize the NS molecules, whereas in striking contrast, they substantially stabilize the PO molecules. The σ effect is much less pronounced in either the NO- or the PS-containing series. The π effect, however, is more unidirectional. Specifically, the π-donating groups contribute positively to the molecular stability in all four isovalent analogues. A semiquantitative analysis, which is based on the frontier molecular orbital theory, is presented. The vastly different responses of the isovalent groups toward the various substituents in their thermal stabilities, as well as their structures, are also discussed.

Introduction

The interest in nitric oxide (NO) has recently exploded when it was discovered to be an important signaling molecule in 1992.[1,2] As a chemical messenger, the short-lived diatomic radical, NO, helps to regulate a diverse array of physiological processes, such as neurotransmission, regulating blood pressure, and preventing blood clots.[3,4] Current research efforts have been focused on understanding the mechanism of the NO production[5−7] and the designing of new drugs which would allow for controllable release of the desired amount of NO pharmaceutically to the various areas of the body.[8]

In this paper, we report a theoretical study of the substituent stabilization effect in a series of NO-containing molecules, RNO, where R is a group of organic and inorganic substituents with various σ- and π-donating/withdrawing abilities. This model study of the bonding energy between the NO group and other elements will shed light on understanding key factors which are involved in affecting the thermal stability of the NO-containing molecules. Furthermore, we believe that the application of our results may potentially contribute to the development of designing new NO production systems.

To conduct a thorough and effective study, we have carried out parallel theoretical investigations in three additional isovalent series, namely, the RNS, RPO, and RPS molecules where R is the same group of substituents. Our approach to evaluating the substituent effect is by computing the electronic energy changes (ΔE) for the following isodesmic reactions:

$$\mathrm{R{-}XY} + \mathrm{H_2} \rightarrow \mathrm{H{-}XY} + \mathrm{RH} \qquad (1)$$

where X stands for the trivalent N or P atom and Y stands for the divalent O or S atom. Because the magnitude of ΔE is a measure of the endothermicity/exothermicity of the entire reaction, its value does not necessarily relate directly to the relative thermal stabilities between R−XY and H−XY, because the energies of H_2 and RH may, conceivably, be very different. However, because the energy difference computed here is for an isodesmic reaction, where the types of the bonds are largely kept unchanged between the reactants and the products, the ΔE value does provide a measure of the size of the interactions between R and the XY group. These interactions, either through bond or through space, would be characteristic between the specific R and XY yet absent in either H−XY or RH. Understanding the correlation between such interactions and the electronic properties of the substituents is the primary goal of the systematic study presented in this manuscript.

Because many types of interactions contribute to the size of ΔE, analysis would be most effective if the ΔE values were compared between related substituents which share much of the same electronic properties but are mainly different in only one component. Hence, the size of the difference between the ΔE values, $\Delta\Delta$E, would provide a better means to evaluate each property individually. Specifically, $\Delta\Delta$E estimates the thermodynamics of the exchange reaction

$$\mathrm{R{-}XY} + \mathrm{R'{-}H} \rightarrow \mathrm{R'{-}XY} + \mathrm{R{-}H} \qquad (2)$$

and its value should directly reflect the difference in the magnitude of the interactions between the XY group and the two different substituents, R and R′. For instance, $\Delta\Delta$E between R = $-CH_3$ and R′ = $-CH{=}CH_2$ would provide a measure primarily of the π effect, as the bonding atoms are the same in the two substituents, as well as most of the electronic properties. Even though the variation in hybridization between the two bonding C atoms in R and R′ may slightly affect the σ-donating ability, this dissimilarity, however, is minute in comparison to the much larger difference in the strength of interactions between the XY group and the substituents, which are, respectively, hyperconjugation and π conjugation. On the other hand, $\Delta\Delta$E

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10.1021/jp014511z CCC: $22.00

TABLE 1: Electronic Energy Change (ΔE) for the Isodesmic Reaction in Eq 1

R	RNO	RNS	RPO	RPS
H	0	0	0	0
CH_3	−12.3	−16.6	−5.6	−8.9
NH_2	−3.9	−11.2	19.5	11.7
OH	−14.2	−32.9	19.3	11.6
F	−19.7	−46.8	23.8	11.9
SiH_3	−7.8	−1.6	−6.6	−4.3
PH_2	−8.2	−8.1	1.2	−0.8
SH	−4.8	−13.7	14.1	8.0
Cl	−8.1	−30.3	17.9	9.3
Br	−2.0	−23.0	20.2	12.5

between R = $-CH_3$ and R′ = $-F$ is expected to give a reasonable estimate of the relative σ effect contributed from the two substituents, because the difference in their π-donating/withdrawing ability is far less than that in their σ-donating/withdrawing ability.[9]

Herein, we report the computational results of the ΔE values for 60 RXY molecules. A semiquantitative molecular orbital (MO) analysis is presented. The frontier MO (FMO) analyses are shown to provide a straightforward explanation of the vastly different ΔE values for the various substituents, as well as the opposite trends of $\Delta\Delta$E, with respect to the σ and π donating/withdrawing ability among the four isovalent series.

Computational Methodology

Our previous studies[9,10] on similar molecules have shown that DFT calculations employing the B3LYP functional have produced structural data in excellent agreement with the experimental data and, therefore, have recommended this method for these studies. All calculations were carried out using the Gaussian 98W suite of programs.[11] Geometries were optimized at the B3LYP[12,13] levels. The basis set employed was 6-311+G(d,p), which is triple-ζ and has included diffuse functions, d polarization functions on the heavy atoms, and p polarization functions on the hydrogen atoms.[14,15] Each stationary point on the potential energy surface was characterized as a minimum by calculations of the vibrational frequencies at the same level of theory, where all of the frequencies were found to be real.

Geometrical parameters, the absolute electronic energies, and bond dissociation energy data for all of the molecules discussed in the paper may be found as Supporting Information.

Results

The ΔE results for the four series of R−XY molecules are listed in Table 1, where XY is one of these four groups: NO, NS, PO, and PS. A total of 10 substituents have been investigated. Among them are two sets of four substituents which have the bonding atoms all from the second row or the third row of the periodic table. The R groups listed in Table 1 are divided into four groups, according to their row number. Comparisons of the ΔE values are made between the R groups with the bonding atoms from the same row, because the relative size of the bonding atoms does affect the R−X bond strength.

Figure 1 shows the ΔE values, which are plotted against the substituents in increasing order of electronegativity of the bonding atom for the eight R groups from the two sets. As the electronegativity of the bonding atom correlates directly with the σ-withdrawing ability of the substituent, the ΔE profiles in Figure 1 project a steady increase of the σ-withdrawing effect across the *x* axis in each series, with the additional π effect of various magnitudes reflected in each substituent as well.

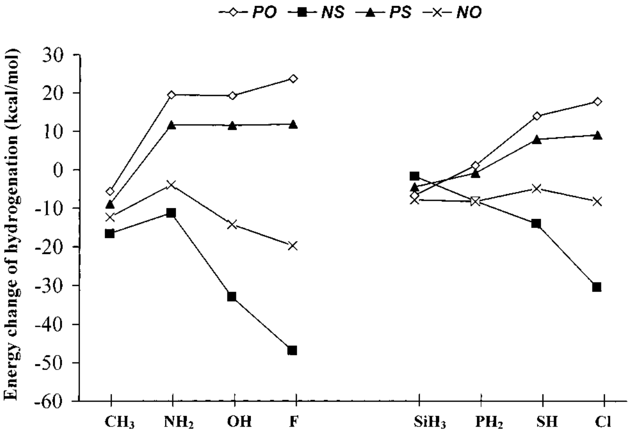

Figure 1. Computed energy change (ΔE) values for the isodesmic reaction of hydrogenation, described in eq 1, as a function of the σ-withdrawing ability of the substituents (R) in R−PO, R−NS, R−PS, and R−NO.

The ΔE profiles for the series with the third-row substituents display consistent patterns. Each set of the four ΔE data points fall more or less on a straight line. In the second-row series, three out of the four ΔE values, which exclude those for the H_2N-XY molecules, are also observed to fit reasonably into a straight line in each series. Furthermore, the ΔE values for the R = NH_2 cases are seen to lie above the imaginary straight line in all four series. Even though there is no physical reason to expect a straight line for the ΔE profile, the ΔE values for all of the H_2N-XY molecules, nevertheless, lie higher than the trend projected by the other three ΔE values according to their σ-withdrawing abilities.

Also observed is that the lines display positive slopes for both the PO and the PS series, while in contrast, a very large negative slope for the NS series. The changes in the ΔE values in the NO series are much smaller, with a slight negative slope for the second-row R groups and a more or less flat line for the third-row substituents.

The ΔE profiles for the third-row substituents display remarkably clear trends. In the NS, PO, and PS series, the ΔE values increase or decrease consistently in all of the series without any exceptions as R becomes more σ withdrawing, from the most σ-donating $-SiH_3$ group to the most σ-withdrawing $-Cl$ group. In the NO series, ΔE oscillates throughout the series with small magnitudes of $\Delta\Delta$E. There is a substantial decrease in ΔE of 28.7 kcal/mol in the NS series, from a slight negative of −1.6 kcal/mol in R = $-SiH_3$ to a large negative of −30.3 kcal/mol in R = $-Cl$. In striking contrast, ΔE increases consistently and dramatically in the PO series, from −6.6 kcal/mol in R = $-SiH_3$ to +17.9 kcal/mol in R = $-Cl$. Compared to the NS and PO series, the span of ΔE is smaller in both PS and NO, with a total $\Delta\Delta$E = 13.6 kcal/mol for the former and even smaller $\Delta\Delta$E of 3.4 kcal/mol for the latter.

Similar trends are repeated in the second-row R groups. First, except for the R = $-NH_2$ cases, the ΔE values increase or decrease consistently from the most σ-donating R = $-CH_3$ molecules to the most σ-withdrawing as in the R = $-F$ cases. Second, the directions of the change in ΔE are also the same as those observed in the third-row analogues, with a large increase of 29.4 kcal/mol in the PO series and a substantial decrease of −32.1 kcal/mol in the NS series. The trends for the NO and the PS series are, again, shown to lie between those for the NS and PO series, with a small positive slope for the former and negative slope for the latter.

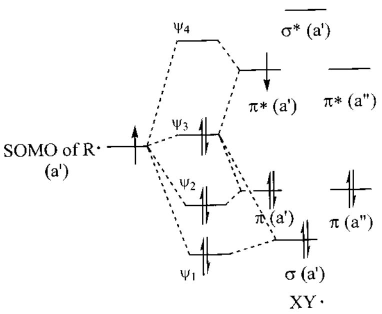

Figure 2. Molecular orbital correlation diagram for the formation of the R−X σ bond. Symmetry allowed interactions are between the SOMO of the substituent and the σ, π, and π^* orbitals of a′ symmetry.

Not only do the ΔE profiles show opposite trends between the X = N and the X = P series, the ΔE values themselves are of the opposite signs as well. Most of the ΔE values in the PO and the PS series are positive. This result suggests that most of the substituents studied here interact with the PO and PS groups in a fashion which stabilizes the PO/PS group more than the H atom does. On the contrary, all of the ΔE values are negative in the NO and NS series, with much larger negative values in the latter. The significantly negative ΔE values, ranging between −23.0 and −46.8 kcal/mol for the halogen and the −OH substituents, indicate that these R groups strongly destabilize the NS group, which, in turn, suggest that these RNS molecules are thermodynamically unstable. These results are consistent with the experimental report that the thionitroso molecules with these substituents have never been synthesized, and the only molecules which have been synthesized or observed spectroscopically with these compositions are the thiazyl molecules.[16−21] In agreement with the experimental reports, calculations have also predicted that the thiazyl forms NSR, with R being a halogen or hydroxyl, are more stable isomers than the nitrosyl forms by a considerable amount of energy. For example, thiazyl fluoride (NSF) has been calculated to be more stable than nitrosyl fluoride (FNS) by −26.2 kcal/mol.[10]

Discussion

The FMO theory offers some insight into the opposite impact, i.e., stabilizing vs destabilizing, of the σ-withdrawing substituent on the XY group between the X = N and X = P series.

Figure 2 presents a FMO correlation diagram, which depicts the formation of the R−X σ bond, labeled as Ψ_3. Symmetry allowed interactions are shown between the singly occupied molecular orbital (SOMO) of R and the MOs in the XY radical, all of which have the a′ symmetry. According to the simplified FMO considerations, the energies of the MOs in the RXY molecule may be calculated as follows, by using the standard variation method:[22]

$$E_1 = [(\epsilon_R + \epsilon_\sigma) - ((\epsilon_R - \epsilon_\sigma)^2 + 4{H_1}^2)^{1/2}]/2 \qquad (3)$$

$$\mathrm{E}_2 = [(\epsilon_R + \epsilon_\pi) - ((\epsilon_R - \epsilon_\pi)^2 + 4{H_2}^2)^{1/2}]/2 \qquad (4)$$

$$E_3 = \epsilon_R + (\epsilon_\sigma - \mathrm{E}_1 + \delta_1) + (\epsilon_\pi - \mathrm{E}_2 + \delta_2) + (\epsilon_{\pi^*} - \mathrm{E}_4) \qquad (5)$$

$$E_4 = [(\epsilon_R + \epsilon_{\pi^*}) + ((\epsilon_R - \epsilon_{\pi^*})^2 + 4{H_3}^2)^{1/2}]/2 \qquad (6)$$

where E_i stands for the energy of the MOs, denoted Ψ_I in Figure 2, ϵ refers to the energy for the interacting orbitals, and H_i is the interaction integral, which measures the coupling strength between the two interacting orbitals (in Figure 2, they are between the SOMO in R and one of the orbitals in XY). Specifically, H_1, H_2, and H_3 respectively refer to the interaction integral between the SOMO of R and the filled σ orbital, the filled π orbital, and the singly occupied π^* orbital of XY. The terms δ_1 and δ_2 in eq 5 account for the increase in energy because of the filled−filled interactions, such as those between the SOMO of R and the filled π or σ orbitals.

According to Figure 2, the stabilization energy which is gained from the formation of the R−X σ bond, SE_σ, is given by

$$SE_\sigma = 2(\epsilon_\sigma - E_1) + 2(\epsilon_\pi - E_2) + (\epsilon_R - E_4) + (\epsilon_{\pi^*} - E_4) \qquad (7)$$

By substituting eqs 3−6 into eq 7

$$SE_\sigma = [(\epsilon_R - \epsilon_{\pi^*})^2 + 4{H_3}^2]^{1/2} - 2(\delta_1 + \delta_2) \qquad (8)$$

Equation 8 shows that SE_σ is a function of three variables, namely, the energy difference between the two SOMOs, $|\epsilon_R - \epsilon_{\pi^*}|$, which is also referred to as the Pauling ionic resonance energy, the coupling strength between the two SOMOs, H_3, and the size of the destabilization energies, δ_1 and δ_2.

The size of δ_1 and δ_2 is dependent on the interaction integrals, H_1 and H_2, respectively, because they arise from the nucleus−nucleus repulsive energy as a result of the interactions between the SOMO in R and the filled σ and π bonding orbitals in the radical XY. According to the second-order perturbation theory, the interaction term, H_i, may be evaluated as, $\langle\phi_A|\hat{H}|\phi_B\rangle^2/\Delta E_{AB}$, where ϕ_A and ϕ_B are the wave functions of the interacting orbitals, H is the coupling Hamiltonian, and ΔE_{AB} refers to the energy difference between the two orbitals.[23] Many factors contribute to the size of the interaction integral; they include the electron populations in ϕ_A and ϕ_B; the size, shape, and orientations of the orbitals; and the matching of the energies of the interacting orbitals. In our discussion, the values of $\langle\phi_A|\hat{H}|\phi_B\rangle$ are assumed to stay more or less constant in a given set of RXY molecules, because all of the R groups contain bonding atoms from the same row. In addition, the SOMO energies in the various R's are greatly different. With this approximation, the analysis is much simplified, and H_i becomes linearly dependent on only ΔE_{AB}^{-1}.

For a specific XY group, ϵ_σ, ϵ_π, and ϵ_{π^*} are all constant. Therefore, as the substituent becomes more σ-withdrawing, the SOMO energy, ϵ_R, decreases. As a result, the Pauling ionic resonance energy would increase, and simultaneously, the sizes of H_1 and H_2 would both be enhanced and that of H_3 would be reduced. The first term contributes positively to SE_σ, whereas the rest of the changes exert the opposite effect. Obviously, according to eq 8, the reduction in H_3 would decrease the value of SE_σ, and for the same reasons, enhanced H_1 and H_2 would increase the values of δ_1 and δ_2. Therefore, the size of SE_σ is determined by the relative magnitude of the three effects. In an extreme case where the interactions between the orbitals are large, such that H_3 is much larger than $|\epsilon_R - \epsilon_{\pi^*}|$, the term $[(\epsilon_R - \epsilon_{\pi^*})^2 + 4{H_3}^2]^{1/2}$ may be approximated as $2H_3$. In such a case, the contribution of the Pauling ionic resonance energy becomes minimal, and the σ-withdrawing substituents are expected to be less favored than the σ-donating groups. On the other hand, if the interaction integrals are all very small, eq 8 can be simplified to $SE_\sigma = \epsilon_R - \epsilon_{\pi^*}$. Under such circumstances, σ-withdrawing R groups will stabilize the RXY molecule more than the σ-donating ones, and the zwitterionic resonance structures, $R^-(XY)^+$ are expected to be a significant contributor to the overall structure of the molecule.

TABLE 2: Mulliken Population Analysis Results for the Partial Charge and Net Spin on X and Y, Where X Is N or P and Y Is O or S

XY	charge on X	charge on Y	net spin on X	net spin on Y
NS	−0.212	0.212	0.634	0.366
NO	−0.09	0.09	0.714	0.286
PS	0.019	−0.019	0.761	0.239
PO	0.256	−0.256	0.852	0.148

Table 2 lists the Mulliken population analysis results for the four XY radicals. For the bonding atoms, there is a large partial negative charge of −0.212 on N in NS and an equally large partial positive charge of 0.256 on P in PO. On the other hand, the electron densities on N in NO and P in PS are both much smaller, with a small negative charge of −0.09 in the former and a very small positive charge of 0.019 in the latter. The net spin data for the bonding atom show an opposite order, with NS < NO < PS < PO. If the net spin values in these XY radicals are considered to correlate directly with the atomic orbital coefficient of the bonding atom in the SOMO π^* orbital, the electron populations for the bonding atoms in the filled orbitals, then, show a definite order of NS > NO > PS > PO, because not only does the face value of the partial charges suggest this order, the reversed order for the spin density will make those bonding atoms bearing large net spin, i.e., P in PO, even more electron deficient in the filled orbitals. This order is further carried through in the size of δ.

Therefore, the largest δ value is expected to occur in the NS series, because of the highest electron density on N in the NS radical. For exactly the opposite reasons, δ should be the smallest in the PO series, as the P atom is the most electron-deficient. Therefore, as the SOMO decreases in the more σ-withdrawing groups, the large gain in δ_1 and δ_2 in the RNS molecules may outweigh the gain in the Pauling ionic resonance energy, and the net result is a decrease in SE_σ. On the other hand, the much smaller increase in δ_1 and δ_2 in the RPO molecules, as R becomes increasingly more σ-withdrawing, may not compete with the increase of $\epsilon_R - \epsilon_{\pi^*}$, and therefore, the total stability energy rises as a result of having the zwitterionic resonance structures contribution of $R^-(P{=}O^+)$. These qualitative analyses are reflected exactly in the ΔE profiles, which show positive trends in the PO series but negative trends in the NS series. Also consistent with the analyses, the amount of destabilizing and stabilizing interactions in RNO and RPS, respectively, are computed to lie between of those in the PO and the NS series.

So far, we have discussed the ΔE profiles as a function of the σ-withdrawing ability. Naturally, the π-donating/withdrawing ability among the substituents is also much different, which should also contribute to affect the ΔE values, in addition to the σ effect.

As the bonding atoms become increasingly σ-withdrawing down the column in Table 1, the substituents become more π-withdrawing as well, except for the $-NH_2$ group. As is known, $-NH_2$ is a much stronger π-donating group than the $-CH_3$, even though the former is more σ-withdrawing. Calculations have shown that the H_2N-XY molecules in their optimized geometries are planar, which suggests that the nitrogen atoms are sp^2-hybridized in order to attain maximum π conjugation. This extra large π conjugation is the reason for the elevated ΔE values observed in Figure 1. It is also understandable that such elevation is not observed in the isovalent $R = -PH_2$ cases, as P does not undergo hybridization; therefore, the involvement in π conjugation of the lone pair electrons in the 3s orbital is expected to be negligible.

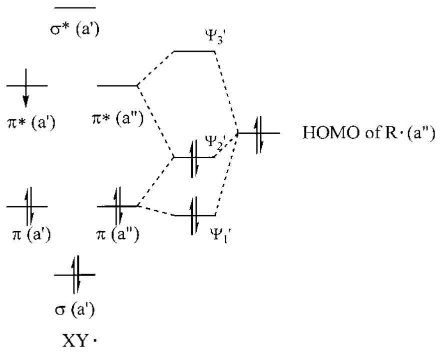

Figure 3. Frontier MO interaction diagram of the π conjugation interactions. The HOMO of R interacts with out-of-plane π and π^* orbitals in XY, where all of the interacting orbitals are of a″ symmetry.

Figure 3 describes the interactions between the orbitals of the a″ symmetry which are responsible for the π-stabilization effect. Specifically, these interactions are between the highest occupied molecular orbital (HOMO) in R and the out-of-plane π (HOMO), as well as the π^* orbital, which is the lowest unoccupied molecular orbital (LUMO) in the radical XY. As a result of the interactions, the energies of the two HOMOs are altered to E_1' and E_2', which can be evaluated by

$$E_1' = [(\epsilon_R' + \epsilon_\pi') - ((\epsilon_R' - \epsilon_\pi')^2 + 4H_1'^2)^{1/2}]/2 \qquad (9)$$

$$E_2' = \epsilon_R' + (\epsilon_\pi' - E_1') + (\epsilon_{\pi^*}' - E_3') + \delta' \qquad (10)$$

$$E_3' = [(\epsilon_R' + \epsilon_{\pi^*}') + ((\epsilon_R' - \epsilon_{\pi^*}')^2 + 4H_2'^2)^{1/2}]/2 \qquad (11)$$

$$SE_\pi = 2(\epsilon_\pi' - E_1') + 2(\epsilon_R' - E_2') \qquad (12)$$

When eqs 9−11 are substituted into eq 12, the expression for SE_π becomes

$$SE_\pi = (\epsilon_R' - \epsilon_{\pi^*}') + [(\epsilon_R' - \epsilon_{\pi^*}')^2 + 4H_2'^2]^{1/2} - 2\delta' \qquad (13)$$

The notations are similar to those in Figure 2, where E_i' stands for the energy for the π MOs in R−XY, labeled as Ψ_I' in Figure 3, ϵ' is the energy for the interacting orbitals, and δ' is the repulsion energy because of the HOMO−HOMO interactions. Parallel to eq 8, eq 11 indicates that three terms contribute to the total size of SE_π, namely, the energy difference between the HOMO in R (ϵ_R') and the LUMO in XY (ϵ_{π^*}'), the HOMO−LUMO interaction integral, H_2, and the value of δ', which is dependent on the magnitude of H_1'. As discussed earlier, the higher-lying HOMO in the π-donating substituents would increase the size of H_2', while simultaneously reducing the sizes of H_1' and δ'. Both of these effects would increase the value of SE_π. The HOMO−LUMO energy difference contributes to SE_π negatively in the term ($\epsilon_R' - \epsilon_{\pi^*}'$) but positively in the term $[(\epsilon_R' - \epsilon_{\pi^*}')^2 + 4H_2'^2]^{1/2}$. Because the contribution of $|\epsilon_R' - \epsilon_{\pi^*}'|$ in the square root term is always smaller than itself, the negative contribution should always outweigh the positive one. Hence, the overall contribution of ($\epsilon_R' - \epsilon_{\pi^*}'$) is negative, with the π-donating groups yielding less negative values. Therefore, dissimilar to the σ effect, π-donating groups are concluded to always contribute positively to SE_π.

To evaluate the π effect, we have carried out calculations for five additional substituents where the bonding atoms are either sp^2- or sp-hybridized. The results are listed in Table 3. In comparison to the $R = -CH_3$ molecules, the ΔE values in the corresponding molecules with $R = -CH{=}CH_2$ all increase

TABLE 3: Electronic Energy Change (ΔE) for the Isodesmic Reaction in Eq 1, Where the Bonding Atoms Are Either sp^2 or sp Hybridized

R	RNO	RNS	RPO	RPS
$CH{=}CH_2$	−3.8	−3.8	0.4	−1.9
$HC{=}O$	−7.0	−5.9	−6.2	−5.7
NO_2	−6.9	−24.3	1.3	−2.3
$C{\equiv}CH$	−15.9	−9.2	1.0	−1.3
$C{\equiv}N$	−23.3	−15.4	−2.8	−4.9

to become less negative. An 8.5 kcal/mol increase is predicted in the NO case, and 12.8, 6.0, and 7.0 kcal/mol increases are computed in the NS, PO, and PS series. As the differences in the σ effect between an sp^3- and an sp^2−C may be considered minor in comparison to the π conjugation available in the vinyl group, these numbers provide a reasonable estimate for the π effect in the four XY groups. The π-donating substituents are shown to stabilize the molecules via π conjugation. The sizes of π conjugation are substantial, as they are all larger than the 3.6 kcal/mol π-conjugation energy in 1,3-butadiene, estimated from the difference in the enthalpy change of hydrogenation reaction between 1-butene and 1,3-butadiene.[24] These results suggest that π conjugation between the vinyl group and these XY groups are all stronger than the isoelectronic $-CH{=}CH_2$ group.

As the π-donating ability decreases down the column from $R = -CH{=}CH_2$ to $R' = -HC{=}O$, ΔE decreases in all four $R'{-}XY$ molecules, ranging from −2.0 kcal/mol in the NS case to −5.8 kcal/mol in the PO case. This is consistent with the previous FMO analysis, in that the π-withdrawing groups always decrease the π stabilization energy (SE$_\pi$), regardless of the specific XY group. In switching to the even more electron-withdrawing $-NO_2$, the change in ΔE is positive in both the PO and PS series but negative in both the NO and NS analogues. The reason for the opposite sign in $\Delta\Delta E$ lies in the fact that $-NO_2$, in comparison to the formyl group, is not only a more π-withdrawing group but a stronger σ-withdrawing group as well. Therefore, the σ effect is, again, at work, as the huge negative ΔE of −24.3 kcal/mol in $O_2N{-}NS$ resulted from the double destabilization effect via both π and σ interactions. The positive $\Delta\Delta E$ of 7.5 kcal/mol in the $O_2N{-}PO$ is, on the other hand, due to the large increase in SE$_\sigma$, which overcomes the decrease in SE$_\pi$.

In the $R = -C{\equiv}CH$ molecules, the second π bond does not show additional π conjugation. This can be readily understood because the additional π orbital is of a′ symmetry. Hence, instead of contributing to the stabilization energy via π conjugation, it, rather, destabilizes the molecule because of the filled−filled interactions with the a′ σ and π orbitals in the XY. The computed results reflect this effect. For example, in comparison with the $R = -CH{=}CH_2$ analogues, the ΔE values for both $HC{\equiv}C{-}NO$ and $HC{\equiv}C{-}NS$ cases are much more negative, with a $\Delta\Delta E$ of −12.1 and −5.4 kcal/mol, respectively. The same destabilization effect is masked by the stabilization effect from a more σ-withdrawing sp-C in the acetyl group, relative to the sp^2−C in the vinyl group in the PO and PS series, and, the ΔE values consequently change very little.

Between the $R = -C{\equiv}CH$ and $R = -C{\equiv}N$ cases, the most dominant difference is the π-donating ability, and therefore, $\Delta\Delta E$ carries the same sign in all four groups, with a higher ΔE value in the acetyl-substituted molecule than the cyano-substituted counterpart.

Finally, the XY bond length results also shed light on the stabilization energy. The connection between the two quantities arises from the fact that the involvement of the antibonding orbitals both brings stability to the molecule and reduces the XY bond order at the same time. Hence, the participation of the π^* orbitals will increase the size of both SE$_\sigma$ and SE$_\pi$ and, simultaneously, lengthen the XY bond.

TABLE 4: XY Bond Length in RXY

R	r_{NO} (Å)	r_{NS} (Å)	r_{PO} (Å)	r_{PS} (Å)
H	1.200	1.576	1.497	1.950
CH_3	1.202	1.576	1.497	1.949
NH_2	1.214	1.616	1.491	1.946
OH	1.166	1.590	1.476	1.933
F	1.128	1.545	1.469	1.909
SiH_3	1.209	1.572	1.504	1.961
PH_2	1.191	1.586	1.495	1.948
SH	1.166	1.592	1.485	1.938
Cl	1.129	1.542	1.474	1.915
Br	1.131	1.534	1.475	1.915

TABLE 5: XY Bond Length in RXY, Where R Contains the Bonding Atoms which Are Either sp^2 or sp Hybridized

R	r_{NO} (Å)	r_{NS} (Å)	r_{PO} (Å)	r_{PS} (Å)
$CH{=}CH_2$	1.215	1.597	1.500	1.955
$HC{=}O$	1.199	1.579	1.498	1.948
NO_2	1.133	1.524	1.472	1.910
$C{\equiv}CH$	1.217	1.604	1.494	1.955
$C{\equiv}N$	1.202	1.593	1.485	1.942

Tables 4 and 5 list the XY bond length for all of the R groups discussed earlier. Consistent with the FMO analysis, XY bond lengths decrease extremely consistently down the column in the PO and PS series, as the bonding orbital becomes more electronegative. The same pattern is mostly repeated in the NO series, except for the $R = -NH_2$ cases, which, as discussed earlier, is caused by the large π conjugations between the lone pair electrons and the π^* (a″) orbital. The trend in the NS bond lengths is, however, not as clear-cut. For instance, among the second-row substituents, the NS bonds are the longest in $R = -NH_2$ and the second longest in $R = -OH$, and among the third-row R groups, the longest NS bond occurs in HS−NS. These results suggest that the π-conjugation effect is larger in the NS series than in any of the other XY cases, which causes the longest XY bonds to occur in molecules with the most π-donating substituents.

Conclusions

We have shown that both the σ and π interactions between the R and the XY groups contribute to affect the thermal stability of the RXY molecules. Specifically, σ-withdrawing groups substantially destabilize the NS group, but significantly stabilize the PO group. The π effect, however, is more unidirectional, with the stronger π-donating groups contributing more positively to the molecular stability in all four isovalent analogues. Both the size as well as the sign of contribution to the stabilizing energy can be explained remarkably well by the semiquantitative analysis based on the FMO theory. We have concluded that the fundamental cause for the drastically different response toward the σ-withdrawing substituents lies in the high electron density on the more electronegative N atom relative to the P atom. There is a close connection between the electron density on the bonding atom and the stabilizing/destabilizing effect of a σ-withdrawing group. As the order for the electron density on the bonding atom is NS > NO > PS > PO, the stabilization energies are in the opposite order, NS < NO < PS < PO, which is in excellent agreement with the calculation results.

Acknowledgment. The support from the SPU Faculty Research Fund is gratefully acknowledged.

Supporting Information Available: Bond dissociation energy data for all of the molecules discussed in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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