The Degree of Rotation Independence of Conjugation of S−N Bonds

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The electron delocalization in π-electron systems is frequently described qualitatively by the concept of conjugation between formal double bonds separated by a formal single bond. In carbon compounds the optimum conjugation usually requires a rather strict, geometrical condition: the exact or near coplanarity of the participating carbon atoms. However, the geometrical conditions are much less strict for third-row atoms if the bonding involves valence-shell d orbitals. In some sulfur compounds, such as *N*-sulfonylsulfilimines, the conjugation is almost unaffected within large ranges of bond-rotation angles, which amounts to rotation-independent conjugation. On the basis of the indications of earlier, limited studies using only minimal basis set and no geometry optimization, in the more extensive present study Density Functional Theory B3LYP calculations using 6-31G* basis set provide more reliable evidence for such flexible conjugation in some sulfur compounds and give an explanation for the experimentally observed interconversion of chiral conformers of *N*-sulfonylsulfilimines.

Introduction

The peculiar properties of many organic sulfur compounds are related to the presence of valence-shell d orbitals and the diffuse electron distribution of the sulfur atom. Sulfur-containing organic molecules often show more unexpected features and a wider range of chemical properties than the analogous carbon compounds. A case of point is the conformational behavior of organic sulfur compounds, where electronic conditions on the stability and on the conformational motions are more flexible and qualitatively different from those of organic compounds involving only the first two rows of the periodic table.

The coplanarity of carbon centers of the delocalized π-electron system is the condition for optimum conjugation in conjugated polyenes such as butadiene. Small distortions from coplanarity of the carbon framework may lead to a reduction of the degree of π-electron delocalization hence to a reduction of conjugation. Some well-known forms of isomerism in such compounds are a direct consequence of the strong preference for coplanarity.

A family of molecules with conjugation involving sulfur atoms being an important factor is that of *N*-sulfonylsulfilimines (for three examples, see Figure 1). In these molecules, the $S^{IV}N$ bond is a formal double bond, separated by the formal single bond NS^{VI} from the two formal double bonds $S^{VI}O$ of the sulfonyl group. This bonding arrangement allows for conjugative interactions in principle. Many chemical and physical properties of these molecules suggest that such conjugation does take place.[1−3] However, these molecules also exhibit some intriguing properties which cannot be explained in terms of the conventional notion of conjugation, typical for π-electron systems involving only second row elements. In particular, crystallographic data, based on X-ray structure determination, show evidence for the presence of two, enantiomeric chiral conformers in the crystal lattice.[4−6] Nevertheless, no actual separation of the two enantiomeric forms has been possible. Note that such a large geometrical difference among carbon compounds almost always implies the existence of two stable and separable isomers. The X-ray results for the solid-state structure of one of the two enantiomers of the $Me_2S^{IV}NS^{VI}O_2Me$ molecule (**I**, *S*,*S*-dimethyl-*N*-methylsulfonylsulfilimine) in Figure 1 clearly show that the structure is chiral. The results of the X-ray structure determination also indicate extensive thermal motion in the solid state, in particular for the methyl groups attached to the S^{IV} atom. Furthermore, NMR studies of the molecule have shown equivalence of the hydrogen atoms in the two methyl groups attached to the S^{IV} atom,[7] although those two methyl groups have different environments in the crystal lattice. To gain more information about this aspect, additional molecules where the methyl group was replaced by a H (or F) atom were also studied in this work.

However, the evident conformational flexibility of molecule **I** appears to be in conflict with additional experimental results, interpreted in terms of the conventional notions of conjugation. The X-ray structure determination[4−6] as well as the IR spectroscopic studies[8] show that the NS^{VI} bond (1.581 Å, in the solid state) is of a strong double-bond character that appears even stronger than the formal double bond $S^{IV}N$ (1.633 Å, in the solid state). On the basis of analogies with conjugated carbon compounds, a short, hence a strong double bond suggests that conformational interconversions, based on $S^{IV}N$ and NS^{VI} bond rotations, are likely to be hindered. Note, however, that any interconversion of the two chiral forms of the molecule must involve extensive distortions with large contributions from both bond-rotation coordinates.

The seemingly conflicting conclusions derived from the experimental findings can be rectified only if one modifies the conventional interpretation of conjugation, originally developed for π-electron systems composed from p orbitals. In the case of the S atom the presence of valence shell d orbitals provides extra flexibility and conjugation may exhibit fundamentally different properties. In particular, the strict geometrical constraints of carbon atom coplanarity for optimum p orbital overlap are in part replaced by those for d−p orbital interactions that

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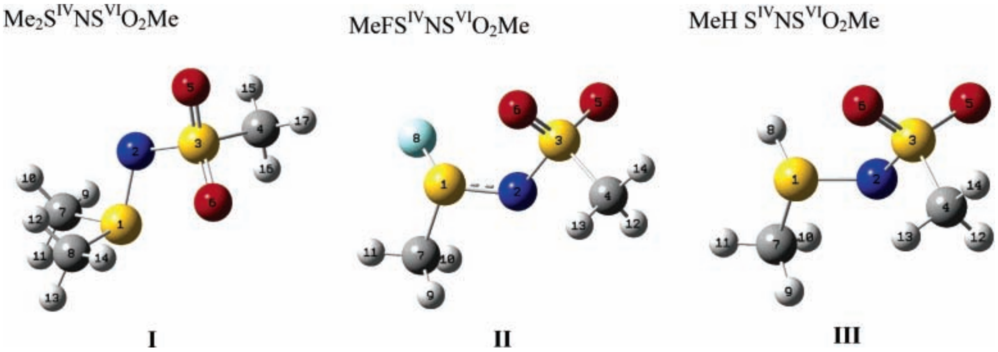

Figure 1. The geometrical structures of molecules containing conjugation of S−N bonds.

are far more versatile geometrically as a consequence of d-orbital orientation. On the basis of semiempirical and low-level HF computations (without geometry optimization) a similar model has been suggested previously in refs 9−12. Note that if the S−N bond system interacts only with carbon-containing π systems, the conjugation is not particularly flexible.[13]

In this paper, we have used full geometry optimization for the analysis of the interrelation between conjugation and bond rotations of the $S^{IV}N$ and NS^{VI} bonds in the $Me_2S^{IV}NS^{VI}O_2Me$ (**I**), $MeFS^{IV}NS^{VI}O_2Me$ (**II**), and $MeHS^{IV}NS^{VI}O_2Me$ (**III**) molecules at the B3LYP/6-31G* level. The initial geometries of these sulfur−nitrogen molecules, used as input for the geometry optimization, are illustrated in Figure 1, and have been based on X-ray structural data.[4−6] The local regions of the potential energy surfaces, the changes in formal atomic charges, and bond populations in the gas phase have been calculated for the two bond rotations about the $S^{IV}N$ and NS^{VI} bonds.

Computational Methods

The minimum energy geometries of the three sulfur compounds were optimized with the ab initio and density functional theory method at the B3LYP/6-31G level. The B3LYP method is a hybrid functional method based on Becke's three-parameter exchange functional[14] with the correlation treatment due to Lee, Yang, and Parr[15] (often labeled as "nonlocal" in the literature). The basis designation 6-31G* refers to a split-valence double-ζ polarization basis set.[16] All the earlier, lower level computations have consistently indicated the presence of rotation-independent conjugation in wide ranges of rotation coordinates, suggesting that the effect is rather dominant, to such an extent that it is manifested already at several, relatively low levels of theory. Nevertheless, we were seeking confirmation using a higher level of theory that is generally regarded highly reliable, certainly for effects that appear consistently dominant at lower levels of theory. The choice of the B3LYP/6-31D* level of theory in the present study is justified by the very wide range of computational experience with this method presented in the literature. The present study complements the earlier semiemperical and Hartree−Fock studies of the problem with a density functional approach, thus providing evidence from a third perspective, in addition to the earlier approaches. IRC calculations[17,18] were performed at the corresponding levels of theory with a coordinate step size of 0.1 $(amu)^{1/2}$ bohr. All calculations were carried out with the Gaussian 03 program package.[19]

Results and Discussion

The optimized geometries of these molecules studied, $Me_2S^{IV}NS^{VI}O_2Me$ (**I**), $MeFS^{IV}NS^{VI}O_2Me$ (**II**), and MeH $S^{IV}NS^{VI}O_2Me$ (**III**) are depicted in Figure 1.

1. $Me_2S^{IV}NS^{VI}O_2Me$. The calculated energy values along the $S^{IV}N$ and NS^{VI} bond-rotation coordinates are presented in Figure 2a. The potential energy curve along the $S^{IV}N$ bond rotation coordinate shows three minima and three maxima. For the bond rotation of $S^{IV}N$, the global minimum point of the potential is found at $\alpha = 220°$. The calculated energy values of the two maxima at rotation angles of 150° and 300° are 10.7 and 7.4 kcal/mol higher than the global minimum, respectively. In the range of the additional two local minima, a 1.1 kcal/mol energy is sufficient for a partially free rotation within the 0−70° interval, which is a narrower valley than the corresponding interval calculated for the NS^{VI} bond rotation. The potential energy curve along the NS^{VI} bond rotation coordinate also shows three minima and three maxima. A rather unusual, wide, and very flat valley was found in the interval $\beta = 50{-}120°$ where the calculated energy variation is very small, merely 0.24 kcal/mol. Another two minima are at $\beta = 0°$ and 170° both with energy 0.102 kcal/mol higher than the global minimum. Within the broader valley large geometry distortions (from 0° to 190°) are possible without requiring energy more than 3.0 kcal/mol, indicating that the actual geometry found in the solid state may well be a consequence of the distorting effects of crystal packing forces. The bond-rotation potential, however, is not flat over the whole 360° range; the energy value of the maximum at rotation angle 270 ° is 9.4 kcal/mol higher than the global minimum.

In general, the small energy variations in one wide angle interval and larger energy variations in the complementing angle interval indicate no major changes of conjugative interactions along the rotated bonds, rather, the actual changes can be attributed to lone pair interactions between the N and O atoms, and to steric interactions between the rotated substituents.

The energy variations found along these bond-rotation coordinates verify that large geometrical distortions are possible without much increase in energy, especially for rotation about the NS^{VI} bond. This is a major difference if compared with the usual properties of conjugated π-electron systems of carbon and other second-row atoms. In the latter systems, minor distortions from the ideal planar arrangement usually cause large energy increases. The results on the calculated conformational flexibility of the two S−N bonds are in accord with experimentally observed racemization of the two chiral conformers found in the crystalline state.

Some aspects of the traditional interpretation of conjugation are often phrased in terms of localized features of electron distributions, such as bond populations and formal atomic charges. Whereas any reduction of the rich information present in a molecular electron density cloud of a rather complicated shape to a few numbers assigned atoms or atom pairs, as is done using any definition of atomic charge or bond population,

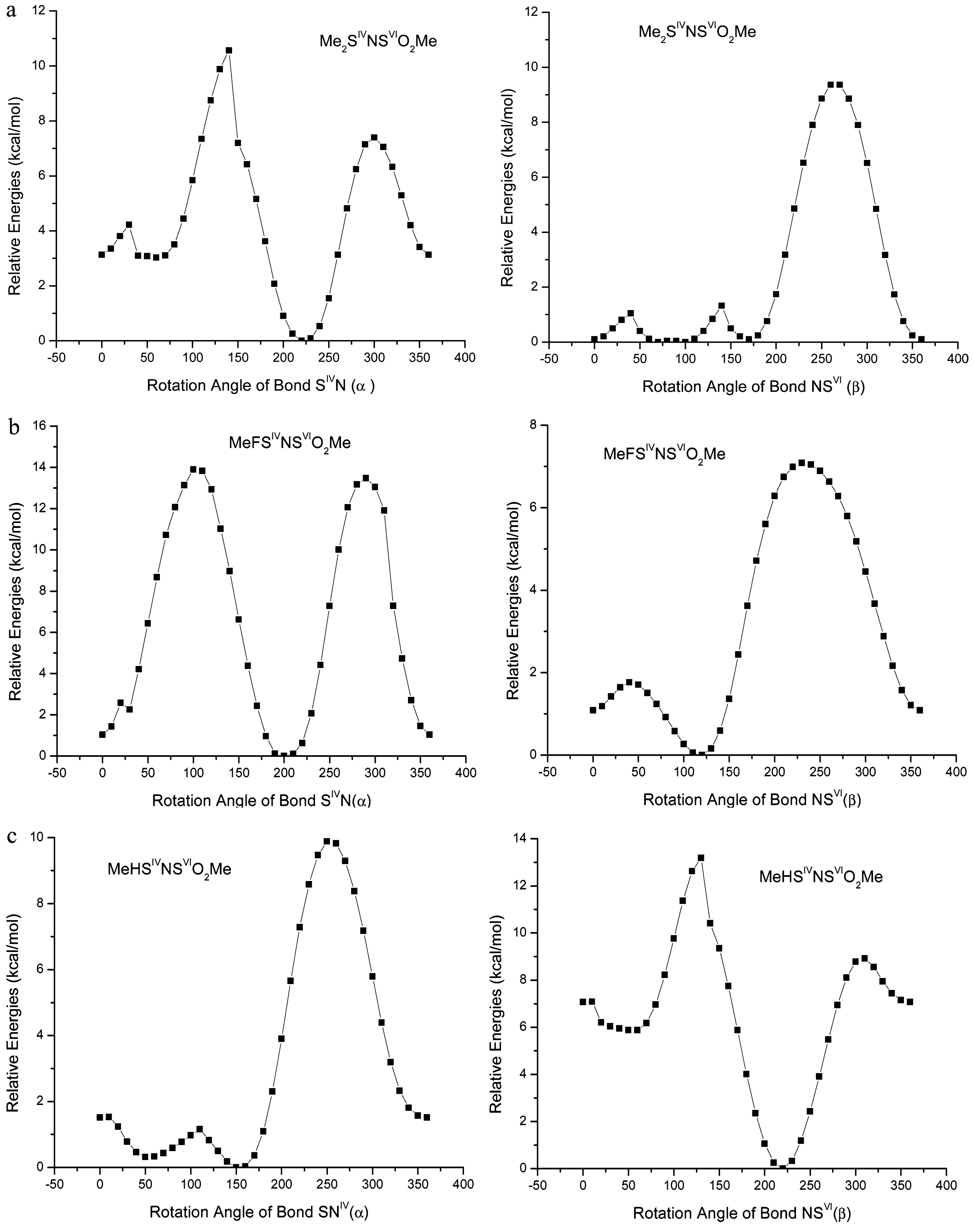

Figure 2. The relative energy values along the $S^{IV}N$ and NS^{VI} bond rotation.

is a drastic simplification, nevertheless, such numbers are often useful to elucidate some trends and correlations. Whereas only cautious conclusions can be based on any definition of atomic charges and bond populations, their variations or stability are certainly indications of the presence or lack of major changes in electron distributions. For this purpose, Mulliken's population analysis is quite sufficient, especially in the context of the (contemporary) concept of conjugation. The degree of variation of bonding patterns can be analyzed by using Mulliken's bond population and charge distribution analysis.

In Figure 3a, the computed bond-population data are plotted as functions of $S^{IV}N$ and NS^{VI} bond-rotation coordinates α and

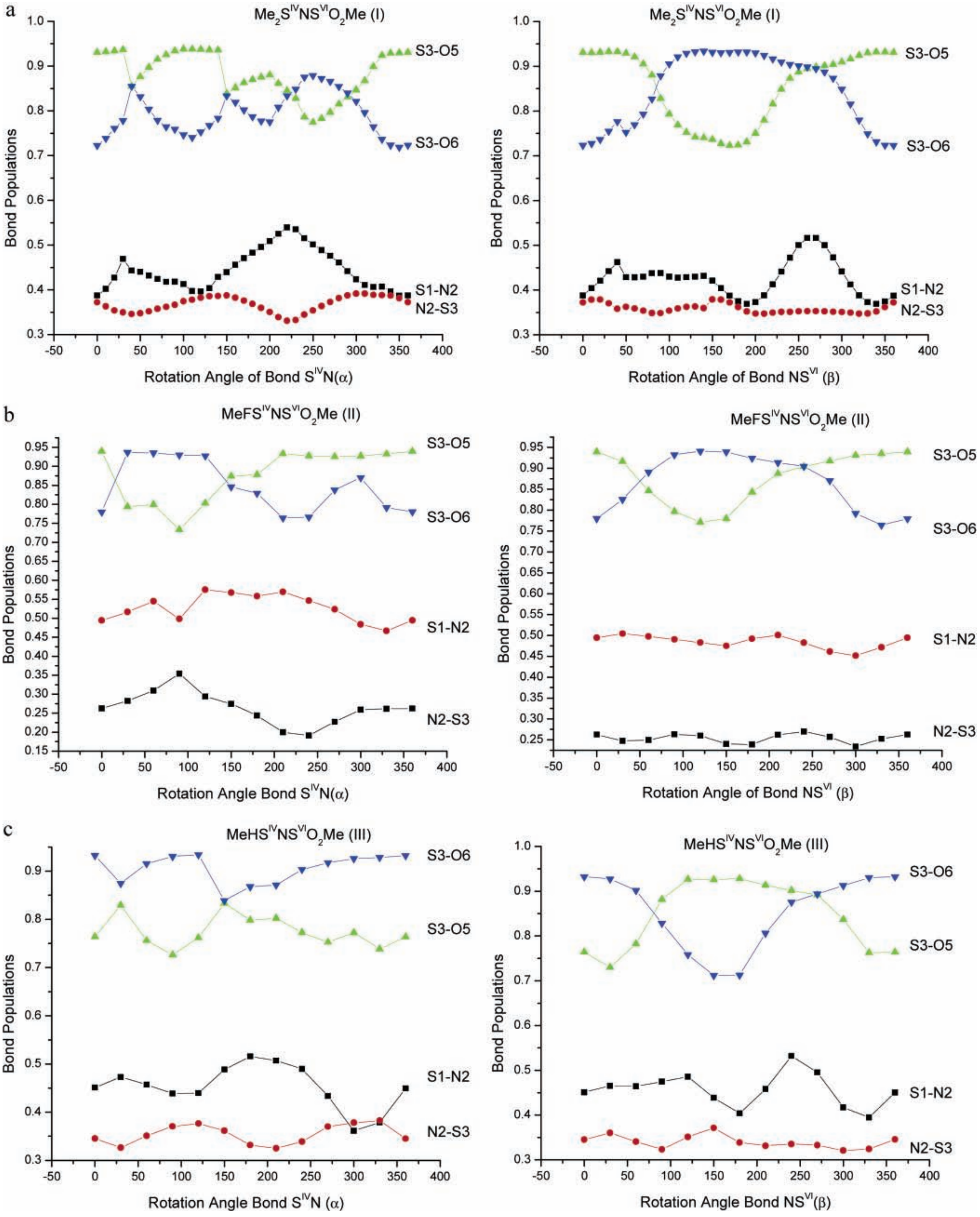

Figure 3. Analysis of Mulliken bond population along the S^{IV}N and NS^{VI} bond rotation.

β. In the analysis of conjugation, the conformation dependence of the following bond populations is important: bonds S^{IV}N-(S1−N2), NS^{VI}(N2−S3), S^{VI}O(S3−O5), and S^{VI}O(S3−O6). The numbers shown in the figures and in parentheses above refer to the serial numbers of the atoms in Figure 1. Both the S^{IV}N and NS^{VI} bond populations are remarkably stable in wide angle intervals, and where larger changes occur, a striking feature of these bond-population functions is their contrary variation for each pair of conjugated bonds. The opposite-phase variations of bond populations are even more pronounced for the two S^{VI}−O bonds along the entire conformational change. As expected, these four bonds appear to be the most affected by the rotations.

The remarkable, opposite-phase population changes for the two S−N bonds, and also for the two S−O bonds, appear as if a compensation would take place within each bond pair. The bond population of one S−N bond changes primarily at the expense of the other, and this compensation is even more evident for the two S−O bonds.

Contrary to some earlier, lower level calculations,[12] where the $S^{IV}N$ bond (a formal double bond) actually has less double-bond character than the formal single bond NS^{VI}, in the present study, the calculated bond population of $S^{IV}N$ is significantly higher than that of NS^{VI} with the exception of a narrow angle range for molecule **III**. Nevertheless, both S−N bonds have rather low bond populations. By contrast, both S−O bonds of the sulfonyl group appear to have strong double-bond character.

Within the family of molecules studied, conjugation is a particular form on non-σ-type electron delocalization, where the region of the NS^{VI} bond, located between two formal double bonds, has a special role. Whereas it seems evident in general that electrons usually delocalize if they have a chance, one can find more direct evidence for conjugation if the NS^{VI} bond between two formal double bonds shows a local π-type contribution. In all conformations, the computed NS^{VI} bond populations are greater than those for NS σ bonds forced to have the same bond length; however, a more direct evidence for π contribution is obtained by actually checking the MO coefficients of those atomic orbitals on the N and S^{VI} centers which have appropriate orientations for π-type contributions. For example, considering the HOMO in all conformations of the flat valley, the AOs with dominant local π-type contributions have MO coefficients of the same sign, and never smaller than 0.315 and 0.084 for N and S^{VI}, respectively. This necessarily means that conjugation through the NS^{VI} bond takes place. Note that if one uses any orbital-based quantum chemical description, any analysis of delocalization must use the computed orbitals as the primary input information, and any further processing of these data cannot add to the physically relevant information content. Hence, within the framework of any orbital-based method, a direct inspection of the orbitals (as one-electron functions) may serve as the ultimate test for delocalization.

In wide angle ranges, the bond-population values change rather little indicating that the formal conjugation between the sulfonyl group and the $S^{IV}N$ bond is not much affected by bond rotations. This feature strongly deviates from the usual behavior of conjugated systems involving only carbon atoms. For the rotation about a formal double bond in the sulfilimine molecule (**I**), a relatively low barrier of approximately 9.0 kcal/mol was obtained, contrary to the much higher value obtained in earlier ab initio calculations.[11]

It is remarkable that the bond population difference is the greatest in the F-substituted molecule (**II**). The highly electronegative F atom apparently reduces the conjugation and helps in establishing a stronger $S^{IV}N$ bond. The calculated formal atomic charges and their variation along the two bond-rotation coordinates are given in Figure 4a. In general, the calculated formal atomic charges are not affected much by bond rotations, the usual deviations from the charges of the optimum geometry are below 0.1 electronic-charge units along the $S^{IV}N$ and NS^{VI} bond-rotation coordinates.

Similar to the conclusions concerning energy variations, the remarkable stability of both the formal atomic charges and the bond populations is an indication of the high level of rotation independence of conjugation, and wherever some actual changes occur in the formal charges, and in particular, in the bond populations, these can be attributed to lone pair interactions between the N and O atoms, as well as to steric interactions among the rotated substituents.

2. Special Features of Molecule $MeFS^{IV}NS^{VI}O_2Me$. Both rotational potentials show two minimum and two maximum energy values along the $S^{IV}N$ and NS^{VI} bond-rotation coordinates (see Figure 2b). The absolute minimum energies are found at $\alpha = 200°$ and $\beta = 120°$ for $S^{IV}N$ and NS^{VI}, respectively. The two maxima of the $S^{IV}N$ rotation at 100° and 300° rotation angles are 13.0 and 12.5 kcal/mol higher than the absolute minimum, respectively; there are no flat ranges on the potential curves at all. Whereas the NS^{VI} bond-rotation potential is not flat, only 1.0 kcal/mol of energy is needed for conversion between the two minima. The relative energy values of the two maxima of the NS^{VI} rotation found at 40° and 230° rotation angles are 1.8 and 7.0 kcal/mol higher than the minimum, respectively.

The calculated bond populations and charge distributions relevant to the analysis of conjugation, involving the $S^{IV}N$, NS^{VI}, and the two $S^{VI}O$ bonds, are shown in Figures 3b and 4b. The results of $MeFS^{IV}NS^{VI}O_2Me$ are not analogous with those of $Me_2S^{IV}NS^{VI}O_2Me$. The calculated formal atomic charges show no obvious correlations with other trends along the $S^{IV}N$ and NS^{VI} bond-rotation coordinates.

3. Special Features of Molecule $MeHS^{IV}NS^{VI}O_2Me$. When one methyl group is replaced by a H atom in $Me_2S^{IV}NS^{VI}O_2$-Me, then both of the potentials show two significant minima and two maxima along the $S^{IV}N$ and NS^{VI} bond-rotation coordinates for $MeHS^{IV}NS^{VI}O_2Me$, although one pair of additional, insignificant minimum and maximum are also found with a very low barrier (see Figure 2c). The nuclear geometry of the calculated absolute minimum energy is found at $\alpha = 150°$ and $\beta = 220°$ for the $S^{IV}N$ and NS^{VI} bond rotations, respectively. In the range of the two local minima of the $S^{IV}N$ rotation, a 1.0 kcal/mol energy is sufficient for a partially free rotation. The NS^{VI} bond-rotation potential, however, is not flat over the whole 360° range: the relative energy values of the two maxima at 130° and 310° rotation angles are 13.0 and 8.8 kcal/mol higher than the global minimum, respectively. The other two minima are found at 60° and 220° for the NS^{VI} bond-rotation coordinates. The local minimum at 60° is 6.0 kcal/mol higher than that at 220°. The rotation is partially free within a narrow (10−70°) interval for the NS^{VI} bond rotation, whereas it is partially free within a wider interval (0−170°) for the $S^{IV}N$ bond rotation. This result differs from that of $Me_2S^{IV}NS^{VI}O_2$-Me.

The conformational dependence of the following bond populations has been computed to elucidate conjugation: bonds $S^{IV}N$, NS^{VI}, and the two $S^{VI}O$ bonds. Just as for $Me_2S^{IV}NS^{VI}O_2$-Me, the conjugation is rotation independent in large rotational intervals for molecule $MeHS^{IV}NS^{VI}O_2Me$. The calculated formal atomic charges and their variation along the two bond-rotation coordinates given in Figures 3c and 4c also indicate a high degree of rotation-independent conjugation.

Conclusions

The bonding patterns of the $Me_2S^{IV}NS^{VI}O_2Me$, $MeFS^{IV}$-$NS^{VI}O_2Me$, and $MeHS^{IV}NS^{VI}O_2Me$ molecules show remarkable quasi-independence of conjugation with respect to the rotations about the $S^{IV}N$ and NS^{VI} bonds in large angle intervals. The

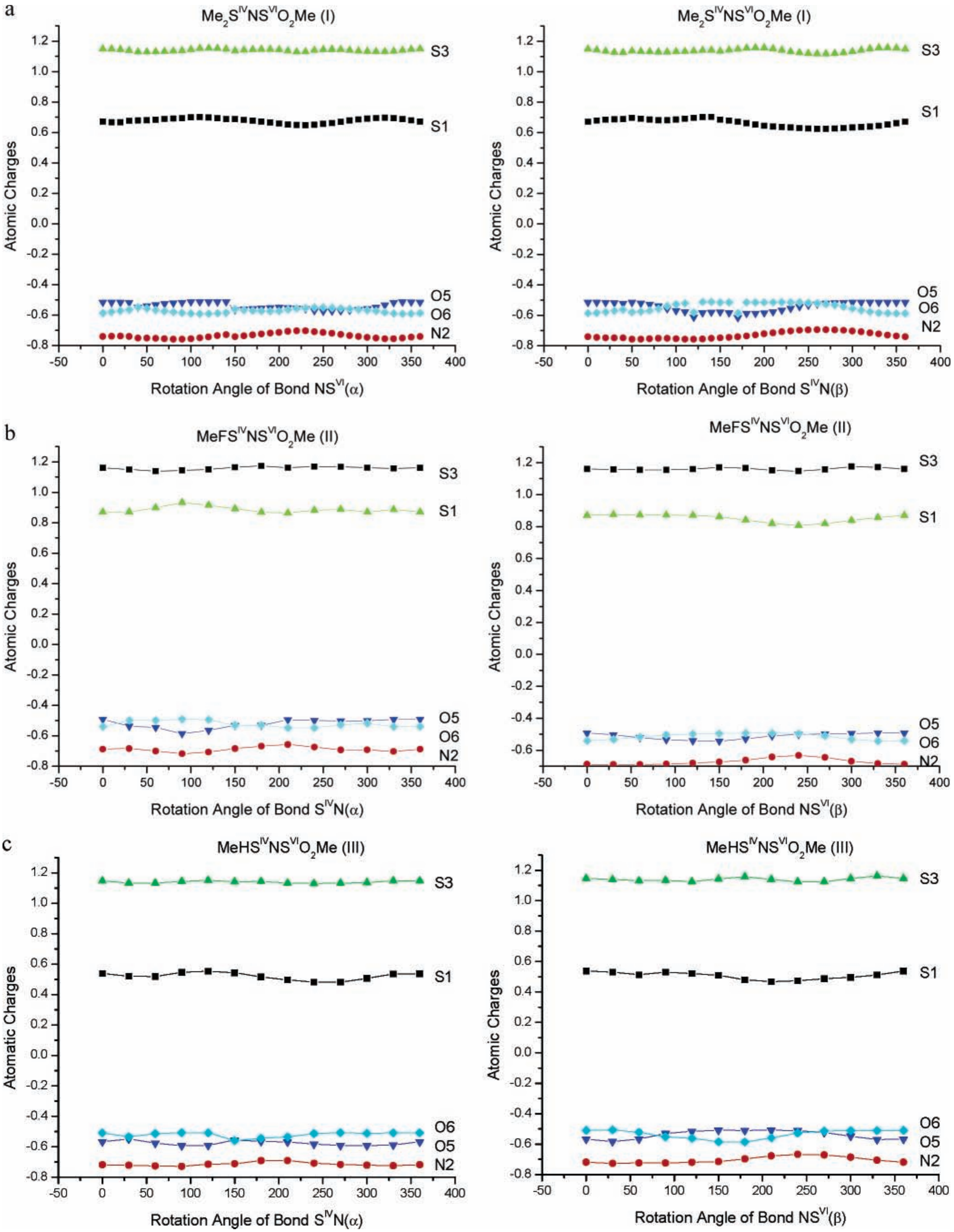

Figure 4. The charge distribution values along the $S^{IV}N$ and NS^{VI} bond rotation.

computed energy variations along the corresponding bond-rotation potentials indicate sufficiently wide low-energy ranges allowing for a low-energy interconversion of the two enantiomeric chiral conformations found in the crystal lattice. The changes of bond populations along bond-rotation coordinates also provide evidence for rotation-independent conjugation. The lack of optical isomerism in solution at room temperature is explained by these results.

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