Structures of the X−Y−NO Molecules and Homolytic Dissociation Energies of the Y−NO Bonds (Y = C, N, O, S)

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High-level theoretical methods (UB3LYP/6-311++g(2df,p), RMP2/6-311++g(d,p), CBS-4M, CBS-Q, and G3) were used to study the structures and bond dissociation energies (BDE) of the X−Y−NO molecules. The data were used to evaluate the previous experimental and theoretical results. It was found that the syn conformation is favored by CH_3−Y−NO, C_2H_5−Y−NO, and CH_3O−Y−NO (Y = C, N, O, S), whereas the anti conformation is favored by CH_3CO−Y−NO and Ph-Y−NO (Y = C, N, O). For Ph−S−NO, the syn conformation is preferred because of the long S−N bond. When X is an alkyl substituent, the Y−NO BDEs increase in the order X−S−NO (~30 kcal/mol) < X−CH_2−NO (~40 kcal/mol) < X−O−NO (~43 kcal/mol) < X−NH−NO (48 kcal/mol). When X is an aromatic substituent, the Y−NO BDEs increase in the order X−O−NO (~21 kcal/mol) < X−S−NO (26 kcal/mol) < X−CH_2−NO (~30 kcal/mol) < X−NH−NO (~35 kcal/mol). The solvent effects of acetonitrile on the free energy change of C−NO and N−NO homolysis are significant, which are about 3−5 kcal/mol. The solvent effects of acetonitrile on the free energy change of O−NO and S−NO homolysis are relatively small, which are about 1−2 kcal/mol. Finally, we found that the remote substituent effects on C−NO, N−NO, O−NO, and S−NO BDEs have ρ^+ values of −0.4~−0.9, 1.7−1.8, 3.2−3.9, and 1.2−1.7 kcal/mol. These values are significantly different from those on the C−H (0.4−0.6 kcal/mol), N−H (3.4−4.6 kcal/mol), O−H (4.1−5.7 kcal/mol), and S−H (2.0−3.8 kcal/mol) BDEs. Therefore, the ground effects are important for the net substituent effects on BDEs.

1. Introduction

Nitric oxide (NO) is a simple intra- and intercellular signaling molecule playing important roles in many human physiological processes.[1] Its biological functions include regulating the blood pressure, transmitting neurostimulation, and participating in the immune systems to kill tumor cells and intracellular parasites. As a free radical, NO is highly reactive in the biological environment. Therefore, to use NO efficiently and safely, the biological systems have to evolve certain NO-carrying vehicles for NO storage, transport, and delivery.

The Y−NO molecules (Y = RCH_2−, RNH−, RO−, or RS−) are possible carriers for NO.[2] They can release the NO molecules through the homolytic bond dissociation at the Y−NO bond. In these Y−NO molecules, the S-nitrosothiols (RS−NO) are especially important, whose role in the uptake, intercellular trafficking, and release of NO in biological systems has been clearly demonstrated with considerable evidence.

Model studies on the Y−NO bond dissociation provides valuable information for the biological NO capture and release. The kinetics and thermodynamics of Y−NO homolysis have been studied with various approaches.[3,4] Recently, Cheng et al. developed a simple experimental method to measure the Y−NO homolytic bond dissociation energies (BDE) in solution.[5] According to this method, the Y−NO BDEs can be derived from the heat of the oxidation reaction $Y{-}H + NO^+ \rightarrow Y{-}NO + H^+$, the p$K_a$ of Y−H, the reduction potential of NO^+ to NO, and the oxidation potentials of Y^- and Y•. Using this method, Cheng et al. have measured the BDEs of N−NO, O−NO, and S−NO bonds.[5]

Although it was claimed in Cheng's work that the homolysis energies should be insensitive to environment because of the cancellation of the solvent effect, in many cases, the solvent effect still significantly changes the homolytic BDEs compared to the gas-phase bond cleavage.[6] Therefore, one must be cautious when using the experimental BDEs from one solvent system to interpret the bond homolysis in the gas phase or other solvents. An additional problem with Cheng's method is the use of both enthalpy and free energy in the same thermodynamic cycle.

Thus, we feel that further studies on the Y−NO BDEs are necessary. In this study, we conducted a high-level theoretical study on a variety of Y−NO systems. The main questions interesting us include the following: 1. What are the structures of the X−Y−NO molecules? 2. What theoretical methods are reliable to predict the Y−NO BDEs? 3. How large are the Y−NO BDEs? 4. How large is the solvent effect on the Y−BDE homolysis? 5. How large is the remote substituent effect on the Y−NO BDEs?

2. Method

All of the calculations were done using Gaussian 98.[8] The geometry was the optimized using UB3LYP/6-31g(d) except for the composite ab initio methods. Because of the double-bond character of Y−NO bond, all of the possible syn and anti conformations were considered for every compound. The most stable conformation was always used for the BDE calculations. In addition, each optimized structure was checked by UB3LYP/6-31g(d) frequency calculations to be a real minimum without any imaginary frequency.

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The single-point energy calculations were done at UB3LYP/6-311++g(2df,p) and ROMP2/6-311++g(d,p) levels. In addition, the standard G3, CBS-Q, and CBS-4M methods were also used in the energy calculation. The gas-phase BDE is defined as the enthalpy change of the following reaction at 298 K in a vacuum:

$$\mathrm{Y{-}NO} \rightarrow \mathrm{Y}^{\bullet} + \mathrm{NO} \qquad (1)$$

The enthalpy of formation for each species was calculated using the following equation:

$$H_{298} = E + ZPE + \Delta H_{298-0} + RT \qquad (2)$$

It should be mentioned that the zero-point energy (ZPE) was calculated at theg UB3LYP/6-31g(d) level scaled by 0.9806. ΔH_{298-0} is the standard temperature correction term including H_{trans}, H_{rot}, and H_{vib}, where $H_{\mathrm{trans}} = {}^{3}/_{2}RT$, $H_{\mathrm{rot}} = {}^{3}/_{2}RT$ (nonlinear) or RT (linear), and H_{vib} is given by standard formulas.

The solvent effects of acetonitrile on the free energy change of Y−NO homolysis were studied using a continuum description of the solvent at UB3LYP/6-311++g(2df,p) and RMP2/6-311++g(d,p) level. The polarized continuum model (PCM) developed by Tomasi[9] was employed. In this PCM model, the atomic radii of the spheres used to build the molecular cavity were adjusted by introducing chemical consideration such as hybridization, formal charge, and first neighbor inductive effect. The effect of the escaped electronic charge outside the cavity was corrected with an additional set of charges on the cavity surface distributed according to the solute electronic density in each point of the surface. Using the method, the mean error with respect to the experimental absolute solvation energies was about 0.2 and 1 kcal/mol for neutral molecules and ions.[9]

It should be mentioned that the standard G3 (Gaussian-3, G3/MP2) theory is a composite ab initio method with geometry optimization at MP2(full)/6-31g(d) level. It uses a scaled HF/6-31g(d) ZPE. A base energy calculated at the MP4/6-31g(d) level of theory is corrected to the QCISD(T)(full)/G3Large level using several additivity approximations at the MP2 and MP4 levels, to take account of more complete incorporation of electron correlation, core correlation, and the effect of a large basis set.

CBS-4M is another composite method. It involves a series of calculations that are designed to recover the errors that result from the truncation of both the one-electron basis set and the number of configurations used for treating correlation energies. The original CBS-4 method uses a single-point HF calculation with a very large basis set (6-311+g(3d2f, 2df, p)) at the HF/3-21g* optimized geometry followed by correction for electron correlation using MP2 and MP4(SDQ) calculations with much smaller basis sets and an extrapolation to the complete basis set. CBS-4M, in contrast to CBS-4, includes the minimal population localization procedure and improved empirical parameters.

The CBS-Q method starts with HF/6-31g* geometry optimization and frequency calculation, which is followed by the MP2(FC)/6-31g* optimization. The single-point energy is calculated at MP2/6-311+g(3d2f, 2df, 2p), MP4(SDQ)/6-31+g(d(f),p), and QCISD(T)/6-31+g* levels. This energy is extrapolated to the complete basis set limit.

3. Results and Discussion

3.1. Conformational Issues. Except for CH_3NO and NH_2-NO, all of the other X−Y−NO molecules have two stable conformations, i.e., syn- or anti-, at the Y−NO bond. The energy difference between the syn- and anti-conformations can be found in Table 1. The typical structures for the syn- and anti-conformations are shown in Figure 1.

TABLE 1: Energy Difference between syn- and anti-X−Y−NO (kcal/mol)[a]

Y	X	UB3LYP/ 6-31g(d)[b]	UB3LYP/ 6-311++g (2df,p)[b]	RMP2/ 6-311++g (d,p)[b]	CBS-4M[c]
CH_2[d]	H	0.0	0.0	0.0	0.0
	CH_3	0.7	0.4	0.5	0.2
	C_2H_5	0.5	0.1	0.3	0.1
	OCH_3	0.8	0.7	0.2	0.1
	$COCH_3$	−1.5	−1.8	−1.6	−1.3
	Ph	−0.3	−0.4	−0.8	−0.1
NH	H	0.0	0.0	0.0	0.0
	CH_3	0.5	0.7	1.3	1.2
	C_2H_5	0.3	0.2	0.5	0.5
	OCH_3	1.2	1.3	2.0	1.8
	$COCH_3$	−3.9	−4.4	−4.3	−4.5
	Ph	−2.4	−2.5	−2.2	−2.6
O	H	−1.0	−1.1	−0.5	−1.1
	CH_3	0.5	0.3	0.3	0.4
	C_2H_5	1.0	0.6	0.7	0.5
	OCH_3	2.1	1.4	1.3	0.9
	$COCH_3$	−1.6	−2.2	−2.6	−3.1
	Ph	−0.9	−1.0	−1.2	−1.3
S	H	−0.8	−1.0	−1.0	−1.1
	CH_3	1.1	0.9	0.7	0.5
	C_2H_5	0.8	0.5	0.6	0.7
	OCH_3	1.4	1.4	2.0	1.7
	$COCH_3$	−1.9	−2.5	−3.0	−4.3
	Ph	0.7	0.5	1.3	0.7

[a] The energy difference is defined as H_{anti} (298 K) − H_{syn} (298 K). Therefore, a positive energy difference in the above table indicates that the syn-conformation is more stable. A negative energy difference indicates that the anti-conformation is more stable. [b] Using UB3LYP/6-31g(d) geometry. [c] Using HF/3-21g* geometry. [d] The anti conformation for XCH_2NO, more precisely, is the gauche conformation.

According to Table 1, it can be seen that the UB3LYP, RMP2, and CBS-4M methods always give the same predictions for the conformation preference. The energy differences between the syn and anti conformations predicted by different methods are also in good agreement with each other.

anti-H−S−NO is about 1 kcal/mol more stable than syn-H−S−NO, presumably because of the steric effect. In comparison, for CH_3S−NO and C_2H_5S−NO, the syn conformation is about 0.5−1 kcal/mol more stable than the anti one. This value is in agreement with the experimental syn → anti free energy change (+1.3 kcal/mol) for methythionitrite.[10] It is also in agreement with the recently reported QCISD(T)/6-311+g* values, 0.78 kcal/mol for CH_3SNO and 0.45 kcal/mol for C_2H_5-SNO.[11] The preference of the syn conformation is possibly due to the formation of a five-member-ring C−H···O hydrogen bond. An alternative explanation might be the hyperconjugation between the σ(C−S) orbital and the σ^*(N−O) orbital or the hyperconjugation between the σ^*(C−S) orbital and the σ(N−O) orbital.[12]

For CH_3O−S−NO, the preference for the syn conformation over the anti one is even stronger (1.4−2.0 kcal/mol). However, for CH_3CO−S−NO, the anti conformation has a lower energy than the syn one by 2−4 kcal/mol presumably because of the steric effect.

According to Table 1, the syn conformation is preferred for PhS−NO, despite the fact that the phenyl group may introduce significant steric effect. The same conformation preference was

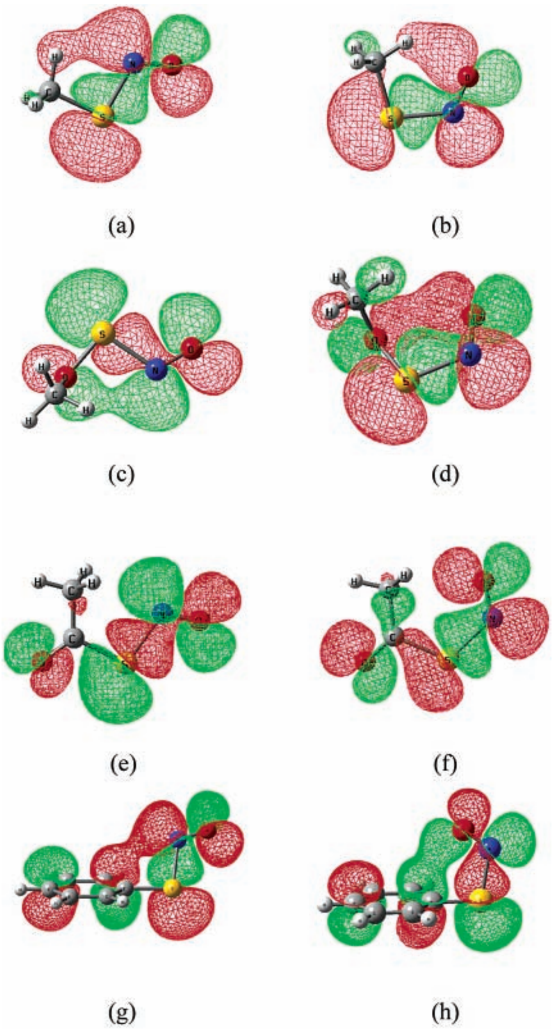

Figure 1. Structures and HOMO of anti-CH_3S-NO (a), syn-CH_3S-NO (b), anti-CH_3OS-NO (c), syn-CH_3OS-NO (d), anti-$CH_3COS-NO$ (e), syn-$CH_3COS-NO$ (f), anti-PhS−NO (g), and syn-PhS−NO (h) obtained using the UB3LYP/6-31g(d) method.

also observed in the crystal structure of *S*-nitroso-4-*tert*-butyl-2,6-bis[(2,2′′,6,6′′-tetramethyl-*m*-terphenyl-2′-yl)methyl]benzenethiol.[13]

For X-CH_2NO, X-NHNO, and X-ONO, the CH_3, C_2H_5, and CH_3O substituents make the syn conformation more stable. In comparison, CH_3CO makes the anti conformation more stable. Interestingly, C_6H_5 also makes the anti conformation more stable, in contrast to the situation for PhS−NO. Presumably, the shorter C−NO, N−NO, and O−NO bonds lead to larger steric effect than the relatively long S−NO bond.

For CH_3CH_2NO, HONO, and CH_3ONO, the energy differences between the syn and anti conformations were measured experimentally (using microwave spectrum) to be 0.5 (syn-CH_3CH_2NO favored),[14] 0.4 (anti-HONO favored),[15] and 0.7 (syn-CH_3ONO favored) kcal/mol,[16] respectively. These values compare reasonably well with our theoretical values, 0.2−0.7, 0.5−1.1, and 0.3−0.5 kcal/mol, respectively.

3.2. Bond Lengths and Angles. In Table 2 are summarized the optimized structures of the X−Y−NO molecules (Y = CH_2, NH, O, or S, only the most stable conformation is considered) calculated using various theoretical methods. From Table 2, one can see that the optimization results from different methods are quite similar to each other.

According to Table 2, the Y−N bond lengths increase in the order N−N (1.33−1.41 Å) < O−N (1.42−1.49 Å) < C−N (1.48−1.52 Å) < S−N (1.72−1.91 Å). This order appears to be the same for the Y−N bond lengths in Y−NH_2, i.e., N−N (1.437 Å) < O−N (1.447 Å) < C−N (1.465 Å) < S−N (1.744 Å) from B3LYP/6-31g(d) optimizations.

The N═O bond lengths increase in the order O−N═O (1.17−1.20 Å) ≈ S−NO (1.17−1.22 Å) < H−N═O (1.207 Å, B3LYP/6-31g(d)) < C−N═O (1.21−1.24 Å) ≈ N−N═O (1.22−1.24 Å). The reason for the shorter N═O bond in O−N═O or S−N═O is caused by the fact that the SOMO energy (RB3LYP/6-31g*) of $H^\bullet$ (−0.07159 au) is significantly higher than that for $SH^\bullet$ (−0.16614 au) or $OH^\bullet$ (−0.18382 au). The SOMO energy for free NO is −0.09425 au. As a result, in XO−NO or XS−NO the contribution from the resonance structure $XO^{-1}N{\equiv}O^{+1}$ or $XS^{-1}N{\equiv}O^{+1}$ is significant, which shortens the N═O bond. On the other hand, the longer N═O bonds in C−N═O and N−N═O should be due to the electron transfer from the XCH_2 or X-NH moiety to the NO π^* antibonding orbital (the one perpendicular to the Y−N═O plane), which results in XCH_2^{+1}-$N-O^{-1}$ or $XNH^{+1}N-O^{-1}$.

3.3. Y-NO BDEs in a Vacuum. In Table 3 are summarized the Y−NO BDEs in a vacuum (Y = CH_2, NH, O, or S) calculated using various theoretical methods.

According to Table 3, G3 and CBS−Q usually provide very similar BDEs, as the largest difference between the results from the two methods is 2.0 kcal/mol only. In comparison, CBS−4M consistently predicts larger Y−NO BDEs than G3 and CBS-Q by 3−6 kcal/mol. The RMP2/6-311++g(d,p) method, on the other hand, consistently predicts lower Y−NO BDEs than G3 and CBS−Q by 2−8 kcal/mol. It should be mentioned that, for the $CH_3CONH-NO$ case, the RMP2/6-311++g(d,p) method predicts an erratically large BDE, 69.1 kcal/mol. The reason for this peculiar result is the unrealistic spin distribution of RMP2 in dealing with nitrogen radicals, which was noticed earlier in a recent paper.[17]

According to Table 3, it appears that the UB3LYP Y−NO BDEs are fairly close to the G3 and CBS-Q ones for the X = H, CH_3, C_2H_5, and OCH_3 cases. However, the UB3LYP methods significantly underestimate the Y−NO BDEs for the X = $COCH_3$ and Ph cases by 1−4 kcal/mol and 3−7 kcal/mol, respectively. This indicates that the UB3LYP methods overestimate the substituent effects on the Y−NO BDEs for the highly conjugated systems. Similar overestimation problems for the substituent effects by the DFT methods were noticed earlier in Radom's work.[18]

The C−NO BDE for CH_3-NO was measured experimentally to be 40.0 ± 0.8 kcal/mol,[19] compared to the G3 (38.0 kcal/mol) and CBS-Q (39.0 kcal/mol) values. The O−NO BDE for HO−NO was determined experimentally to be 49.3 kcal/mol,[19] which is also in good agreement with the G3 (48.1 kcal/mol) and CBS-Q (50.1 kcal/mol) values. In addition, excellent agreements are found for CH_3O-NO (exp, 41.8 ± 0.9 kcal/mol;[19] G3, 42.4 kcal/mol; CBS-Q, 43.9 kcal/mol) and C_2H_5O-NO (exp, 42.0 ± 1.3 kcal/mol;[12] G3, 42.8 kcal/mol; CBS-Q, 44.4 kcal/mol).

Thus, from the above comparisons, we conclude that the G3 and CBS-Q methods could provide reliable Y−NO BDEs with an error bar about 1−2 kcal/mol. CBS-4M tends to overestimate the Y−NO BDEs, whereas RMP2 underestimates them. UB3LYP also underestimate the Y−NO BDEs for the highly conjugated systems.

According to the G3 and CBS-Q results, the C−NO BDEs are 38−40 kcal/mol for CH_3-NO, CH_3CH_2-NO, and C_2H_5-CH_2-NO. The C−NO BDEs for CH_3OCH_2-NO, CH_3COCH_2-

TABLE 2: Optimized Bond Lengths (Å) and Bond Angles (Degrees) for X−Y−NO

		UB3LYP/6−31 g(d)			CBS-4M[a]			CBS-Q[b]			G3[c]		
Y	X	*r*(Y−N)	*r*(N−O)	∠YNO	*r*(Y−N)	*r*(N−O)	∠YNO	*r*(Y−N)	*r*(N−O)	∠YNO	*r*(Y−N)	*r*(N−O)	∠YNO
CH_2	H	1.488	1.211	113.1	1.499	1.217	112.7	1.486	1.223	112.5	1.479	1.235	112.3
	CH_3	1.500	1.211	113.8	1.509	1.216	113.7	1.497	1.222	113.3	1.490	1.234	113.1
	C_2H_5	1.499	1.212	113.9	1.506	1.217	113.7	1.496	1.222	113.4	1.489	1.235	113.2
	OCH_3	1.494	1.208	114.0	1.492	1.211	114.5	1.491	1.219	113.5	1.483	1.232	113.3
	$COCH_3$	1.498	1.209	113.0	1.495	1.215	112.7	1.492	1.222	112.4	1.483	1.235	112.2
	Ph	1.517	1.208	112.9	1.508	1.215	112.6	1.498	1.223	112.1	1.493	1.236	111.9
NH	H	1.339	1.221	113.6	1.349	1.228	113.6	1.341	1.224	113.3	1.341	1.236	113.0
	CH_3	1.335	1.228	113.6	1.338	1.235	113.7	1.335	1.232	113.3	1.334	1.244	112.9
	C_2H_5	1.338	1.228	114.4	1.337	1.237	114.3	1.337	1.232	114.0	1.337	1.244	113.6
	OCH_3	1.362	1.215	114.9	1.412	1.208	114.0	1.368	1.219	114.3	1.367	1.232	114.0
	$COCH_3$	1.371	1.214	116.0	1.376	1.217	116.4	1.369	1.219	115.9	1.367	1.232	115.6
	Ph	1.340	1.225	113.1	1.347	1.228	113.5	1.340	1.230	112.9	1.339	1.242	112.6
O	H	1.427	1.179	110.6	1.442	1.179	110.2	1.416	1.184	110.7	1.423	1.197	110.3
	CH_3	1.397	1.191	114.4	1.409	1.192	113.6	1.388	1.198	114.5	1.392	1.210	114.1
	C_2H_5	1.395	1.192	114.6	1.406	1.194	113.7	1.387	1.199	114.6	1.391	1.211	114.2
	OCH_3	1.448	1.174	115.0	1.465	1.172	114.0	1.494	1.170	114.2	1.484	1.184	114.0
	$COCH_3$	1.488	1.167	109.3	1.460	1.170	109.4	1.526	1.164	109.2	1.509	1.180	109.0
	Ph	1.474	1.172	109.9	1.462	1.172	109.4	1.491	1.171	110.1	1.477	1.187	109.8
S	H	1.913	1.175	115.1	1.758	1.208	113.8	1.901	1.180	115.0	1.842	1.205	114.1
	CH_3	1.865	1.187	116.6	1.732	1.213	118.4	1.850	1.192	116.7	1.775	1.224	115.1
	C_2H_5	1.864	1.188	116.7	1.720	1.219	117.1	1.821	1.200	116.0	1.783	1.222	115.8
	OCH_3	1.849	1.190	114.6	1.684	1.224	118.3	1.798	1.205	114.9	1.756	1.226	115.2
	$COCH_3$	1.894	1.180	114.3	1.741	1.211	113.9	1.882	1.187	114.1	1.827	1.211	113.6
	Ph	1.927	1.176	115.9	1.750	1.208	117.5	2.048	1.162	113.4	1.913	1.195	114.4

[a] Equivalent to the HF/3-21g* optimization. [b] Equivalent to the MP2(FC)/6-31g* optimization. [c] Equivalent to the MP2(full)/6-31g(d) optimization.

TABLE 3: Y−NO BDEs of X−Y−NO (kcal/mol)

Y	X	UB3LYP/ 6-31g(d)	UB3LYP/ 6-311++g(2df,p)[a]	RMP2/ 6-311++g(d,p)[a]	CBS-4M	CBS-Q	G3
CH_2	H	38.7	36.2	34.5	44.0	39.0	38.0
	CH_3	37.8	35.1	36.0	44.7	40.2	39.4
	C_2H_5	38.1	35.3	36.4	44.9	40.9	39.8
	OCH_3	32.5	29.9	31.0	40.0	35.2	34.2
	$COCH_3$	27.7	25.7	28.5	37.2	31.1	30.4
	Ph	23.7	21.5	27.3	31.1	30.2	29.6
NH	H	48.0	46.7	43.7	52.1	47.7	45.7
	CH_3	46.6	45.2	45.6	53.7	49.0	47.3
	C_2H_5	46.5	44.9	45.7	53.8	49.1	47.7
	OCH_3	25.4	24.3	24.9	32.7	26.8	26.1
	$COCH_3$	47.6	46.1	69.1	56.8	51.2	49.9
	Ph	33.8	31.9	35.6	38.8	36.1	34.2
O	H	49.4	47.3	45.1	52.9	50.1	48.1
	CH_3	40.1	36.7	43.5	47.3	43.9	42.4
	C_2H_5	40.7	37.5	44.4	47.0	44.4	42.8
	OCH_3	22.6	19.9	24.7	34.5	26.0	24.7
	$COCH_3$	28.2	27.0	22.8	28.3	26.8	25.2
	Ph	17.4	15.5	14.4	26.2	22.6	20.8
S	H	28.9	29.1	20.4	32.8	30.8	28.9
	CH_3	29.6	29.7	22.5	34.4	33.7	31.5
	C_2H_5	29.1	30.8	24.2	34.4	33.3	31.5
	OCH_3	21.9	22.9	16.9	29.1	26.9	25.7
	$COCH_3$	23.9	23.7	18.8	30.1	28.0	26.6
	Ph	20.4	21.1	18.4	27.7	26.6	25.4

[a] Using UB3LYP/6-31g(d) geometries.

NO, and $PhCH_2$−NO are significantly smaller because of the radical stabilization effects of the OCH_3, $COCH_3$, and Ph groups.

The N−NO BDEs are 46−49 kcal/mol for NH_2−NO, CH_3-NH−NO, and C_2H_5NH−NO. CH_3ONH−NO and PhNH−NO have significantly smaller N−NO BDEs because of the radical stabilization effects of the OCH_3 and Ph groups. However, the $COCH_3$ group is a destabilization substituent for the nitrogen radical, which was discussed in detail in our earlier paper.[17] Therefore, the N−NO BDE of CH_3CONH−NO is 50−51 kcal/mol, which is about 3−4 kcal/mol larger than that for NH_2−NO.

The O−NO BDEs are 48−50 kcal/mol for HO−NO. CH_3O−NO and C_2H_5O−NO have significantly smaller BDEs (42−44 kcal/mol), indicating that the radical stabilization effects of the CH_3 and C_2H_5 groups on the stability of an oxygen radical are much more significant than the carbon and nitrogen cases. Also, CH_3OO−NO, CH_3COO−NO, and PhO−NO have much smaller O−NO BDEs than HO−NO, indicating the strong radical stabilization effects of the OCH_3, $COCH_3$, and Ph groups on the oxygen radical.

The S−NO BDEs of HS−NO are 29−31 kcal/mol, which is close to the S−NO BDEs of CH_3S−NO and C_2H_5S−NO. Therefore, the radical stabilization effects of the CH_3 and C_2H_5 groups on the stability of a sulfur radical are not strong. CH_3-OS−NO, CH_3COS−NO, and PhS−NO have slightly smaller

TABLE 4: Solvent Effects of Acetonitrile on the Free Energy Change of Y−NO Homolysis (kcal/mol)

Y	X	UB3LYP/ 6-311++g(2df,p)[a]	RMP2/ 6-311++g(d,p)[a]
CH_2	H	4.3	4.8
	CH_3	2.8	3.4
	C_2H_5	2.5	2.6
	OCH_3	4.3	4.0
	$COCH_3$	3.0	2.1
	Ph	4.2	5.3
NH	H	4.7	4.4
	CH_3	3.3	3.9
	C_2H_5	4.5	3.4
	OCH_3	3.7	2.8
	$COCH_3$	2.1	1.7
	Ph	3.1	3.1
O	H	1.5	1.4
	CH_3	0.9	0.8
	C_2H_5	1.0	0.9
	OCH_3	0.5	0.4
	$COCH_3$	1.2	1.1
	Ph	1.0	1.1
S	H	1.3	1.4
	CH_3	1.0	1.0
	C_2H_5	1.1	0.9
	OCH_3	1.6	1.3
	$COCH_3$	1.4	1.1
	Ph	1.5	2.9

[a] Using UB3LYP/6-31g(d) geometries. The solvent effect is defined as solvent effect = ΔG (homolysis in solvent) − ΔG (homolysis in a vacuum).

SCHEME 1

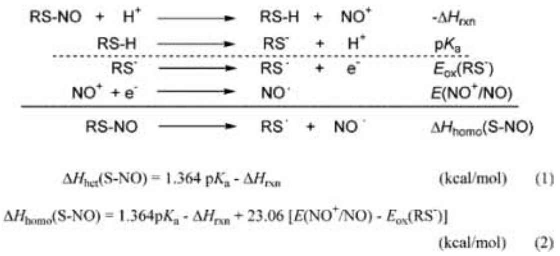

TABLE 5: BDEs of Y−NO Bonds Calculated for 4-X−C_6H_4−Y−NO (kcal/mol)[a]

	Y = CH_2		Y = NH		Y = O		Y = S	
X	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
H	21.5	27.3	31.9	35.6	15.5	14.4	21.1	18.4
CH_3	21.4	27.3	31.1	34.8	13.8	13.1	20.5	18.0
NH_2	21.1	27.0	28.2	32.5	8.7	8.9	18.0	16.8
OH	21.3	27.2	29.3	33.4	11.4	10.9	19.5	17.4
F	21.3	27.2	30.6	34.5	13.9	13.0	20.6	18.1
CN	19.5	26.2	31.4	35.7	16.1	15.6	21.3	19.0
COOH	20.0	26.6	32.1	36.1	16.6	15.4	21.2	18.8
NO_2	19.3	26.4	32.2	36.3	17.8	15.7	22.3	19.8
ρ^{+b}	−0.9	−0.4	1.8	1.7	3.9	3.2	1.7	1.2
r^c	0.75	0.68	0.92	0.96	0.97	0.98	0.96	0.98

[a] B3LYP means that the result is obtained at UB3LYP/6-311++g(2df,p)//UB3LYP/6-31g(d) level. MP2 means that the result is obtained at RMP2/6-311++g(d,p)//UB3LYP/6-31g(d) level. [b] The slope of the correlation between BDEs and the substituent σ_p^+ constants. [c] The correlation coefficient of the correlation between BDEs and the substituent σ_p^+ constants.

S−NO BDEs, because the radical stabilization effects of the corresponding substituents.

3.4. Solvent Effects on Y−NO Homolysis. Cheng et al. reported that the S−NO BDE for PhS−NO (in acetonitrile) is 19.4 ± 1.3 kcal/mol, which appeared to agree with their B3LYP/6-31+g* result (in a vacuum), 20.2 kcal/mol.[5e] However, our G3 and CBS-Q predictions (in a vacuum) for the same BDE are 25.4 and 26.6 kcal/mol, which are 5−6 kcal/mol larger than Cheng's values.

We wonder if the solvent effect is large for the homolysis. Thus, we used PCM model to calculate the solvent effects on the free energy change of Y−NO homolysis. (Table 4) The results show that the free energy change of Y−NO homolysis in acetonitrile is always larger than that in a vacuum.

A detailed examination of the results reveals that the solvent effects on the free energy change of C−NO and N−NO homolysis are as large as 3−5 kcal/mol, which is about 1/10 of the free energy change of C−NO and N−NO homolysis in a vacuum. In comparison, the solvent effects on the free energy change of O−NO and S−NO homolysis are around 1 kcal/mol, which is smaller than 1/20 of the free energy change of O−NO and S−NO homolysis in a vacuum.

The small solvent effect on the free energy change of the S−NO homolysis suggests that the 5−6 kcal/mol difference between our calculation and Cheng's measurement on S−NO BDE in a vacuum is not from the solvent effects. The likely reason for the experimental underestimation is the questionable use of both enthalpy and free energy in the same thermodynamic cycle in Cheng's measurement.

In fact, according to Cheng's method,[5] the S−NO BDE was calculated using the thermodynamic cycle shown in Scheme 1. In this cycle, ΔH_{rxn} is the enthalpy change, but pK_a and E correspond to free energy changes. Therefore, the empirical equation for the homolytic BDE (an enthalpy change) is only valid when the solvent effects on the entropy part of pK_a and E are constant for the whole series of systems. However, for highly polarized species such as RS and RS^-, the solvent reorganization contribution to the entropy must be large and highly variable depending on the nature of R. As a result, use of the thermodynamic cycle in Scheme 1 is problematic.

3.5. Remote Substituent Effects on Y−NO BDEs. The remote substituent effect on the homolytic BDEs is an interesting problem. In Cheng's study, they determined the Y−NO BDEs of some substituted phenol systems, from which they conducted Hammett regressions against the electronic substituent constants.[5] Herein, we would like to compare our theoretical substituent effect with the experimental results. Therefore, we calculated the Y−NO BDEs of a number of para-substituted phenyl systems. The results are listed in Table 5.

We only used the UB3LYP/6-311++g(2df,p) and RMP2/6-311++g(d,p) methods to calculate the substituent effects on Y−NO BDEs because of the size of the system. Although from previous results it appears that UB3LYP tends to overestimate the substituent effects on Y−NO BDEs, from the results in Table 3, one can see that the RMP2 method predicts fairly accurate substituent effects for all of the systems. A similar good performance of the RMP2 method in calculating the substituent effects on BDEs (except for the nitrogen radicals where RMP2 may give erratic results[17]) was also seen by Radom et al.[7] Therefore, use of UB3LYP and RMP2 methods together may still provide reliable and valuable information on the substituent effects.

According to Table 5, the remote substituent effects on the C−NO BDEs show a negative correlation with the substituent σ_p^+ constants. Although the correlation coefficient (r) is fairly poor (0.68−0.75), the validity of the negative correlation could be directly seen in Figure 2. In addition, the slope (ρ^+) of the regression is not negligible (−0.4∼−0.9 kcal/mol).

In comparison, the N−NO, O−NO, and S−NO BDEs all show significant and positive correlation with the substituent

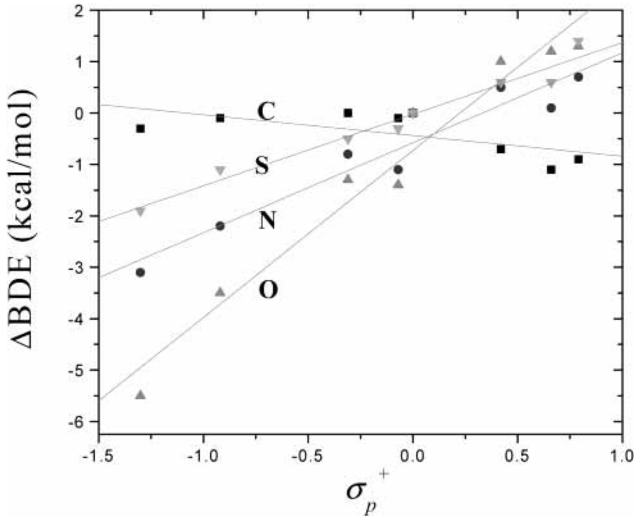

Figure 2. Regressions between the Y−NO BDEs and the substituent σ_p^+ constants for 4-X−C_6H_4−Y−NO.

TABLE 6: BDEs of Y−H Bonds Calculated for 4-X−C_6H_4−Y−H (kcal/mol)[a]

	Y = CH_2		Y = NH		Y = O		Y = S	
X	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
H	86.4	88.3	88.2	92.2	83.4	81.5	76.4	75.0
CH_3	86.0	88.0	86.7	91.1	81.2	79.8	75.1	74.2
NH_2	84.7	87.3	82.2	87.9	74.7	74.9	71.3	73.0
OH	85.6	87.8	84.4	89.4	78.2	77.2	73.0	72.9
F	86.4	88.4	86.9	91.4	81.5	79.7	75.2	74.2
CN	85.8	88.4	90.7	94.3	85.5	83.3	78.2	76.2
COOH	85.8	88.3	90.8	94.1	85.9	83.0	78.3	76.1
NO_2	85.8	88.7	92.4	95.0	87.6	83.4	79.8	77.0
ρ^{+b}	0.4	0.6	4.6	3.4	5.7	4.1	3.8	2.0
r^c	0.55	0.94	0.99	0.99	0.99	0.98	0.99	0.96

[a] B3LYP means that the result is obtained at UB3LYP/6-311++g(2df,p)//UB3LYP/6-31g(d) level. MP2 means that the result is obtained at RMP2/6-311++g(d,p)//UB3LYP/6-31g(d) level. [b] The slope of the correlation between BDEs and the substituent σ_p^+ constants. [c] The correlation coefficient of the correlation between BDEs and the substituent σ_p^+ constants.

σ_p^+ constants. The r values are fairly good (0.92−0.98). The ρ^+ values are relatively large (1.7−1.8 kcal/mol for N−NO, 3.2−3.9 kcal/mol for O−NO, and 1.2−1.7 kcal/mol for S−NO). It should be mentioned that using Cheng's experimental S−NO BDEs one can obtain a ρ^+ value of −1.8 kcal/mol (r = 0.86) for 4-X−C_6H_4−S−NO. However, using Cheng's theoretical S−NO BDEs from B3LYP/6-31+g* calculations, one can obtain a ρ^+ value of +1.5 kcal/mol (r = 0.94). The latter is in agreement with our results.

3.6. Comparison of the Substituent Effects on Y−NO BDEs and Y−H BDEs. Pratt et al. recently proposed that when X has significant effects on Y−Z BDEs in 4-X−C_6H_4−Y−Z it must be due to their stabilization or destabilization of the radicals instead of the neutral compounds regardless of the nature of X, Y, and Z.[20] Quantitatively, this means that

$$\mathrm{BDE}(4\text{-}XC_6H_4Y{-}Z_a) - \mathrm{BDE}(C_6H_5Y{-}Z_a) \approx \mathrm{BDE}(4\text{-}XC_6H_4Y{-}Z_b) - \mathrm{BDE}(C_6H_5Y{-}Z_b) \quad (3)$$

If the above equation were valid, one would expect that the remote substituent effects on Y−NO BDEs and Y−H BDEs should be the same.

We calculated the Y−H BDEs for the same groups of substituted phenyl systems. The results are shown in Table 6. Comparing Tables 5 and 6, one can see that the remote substituent effects on Y−NO BDEs are significantly different from those on Y−H BDEs. The ρ^+ value for C−H BDEs is 0.4−0.6 kcal/mol, which is about 1.0−1.3 kcal/mol larger than that for C−NO. The ρ^+ value for N−H BDEs is 3.4−4.6 kcal/mol, which is about 1.7−2.8 kcal/mol larger than that for N−NO. The ρ^+ value for O−H BDEs is 4.1−5.7 kcal/mol, which is about 0.9−1.8 kcal/mol larger than that for O−NO. The ρ^+ value for S−H BDEs is 2.0−3.8 kcal/mol, which is about 0.8−2.1 kcal/mol larger than that for S−NO.

Therefore, Pratt's proposal is not correct. Because the Y−NO and Y−H bond dissociation results in the same radicals, the different substituent effects must be caused by the stabilization or destabilization effects of the substituents on the intact Y−NO and Y−H bonds before homolysis.

3.7. Origin of the Substituent Effects. To understand the origin of the different substituent effects on the Y−NO and Y−H BDEs, we calculated the enthalpy changes of the following isodesmic reactions

$$X{-}C_6H_4{-}Y{-}Z + C_6H_6 \rightarrow X{-}C_6H_5 + C_6H_5{-}Y{-}Z \ (Z = NO \text{ or } H) \quad (4)$$

$$X{-}C_6H_4{-}Y^\bullet + C_6H_6 \rightarrow X{-}C_6H_5 + C_6H_5{-}Y^\bullet \quad (5)$$

We call the enthalpy changes of eq 4 the ground effects, because they reflect the energetic consequence of separating the remote substituent (X) from the Y−NO or Y−H moiety. We call the enthalpy changes of eq 5 the radical effects, because they reflect the energetic consequence of separating X from the radical center, $Y^\bullet$. It should be noted that the substituent effects on the

TABLE 7: Ground Effects and Radical Effects Calculated Using UB3LYP/6-311++G(2df,p)//UB3LYP/6-31g(d) Method (kcal/mol)[a]

X	CH_2−NO	CH_2−H	$CH_2^\bullet$	NH−NO	NH−H	$NH^\bullet$	O−NO	O−H	$O^\bullet$	S−NO	S−H	$S^\bullet$
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_3	0.1	−0.2	0.2	0.0	−0.7	0.8	0.0	−0.5	1.7	0.5	−0.1	1.1
NH_2	0.5	−0.7	1.0	−0.4	−2.7	3.3	−0.3	−2.2	6.5	1.8	−0.2	4.9
OH	0.0	−0.5	0.2	−0.9	−2.2	1.6	−0.7	−1.9	3.4	0.7	−1.0	2.4
F	−0.5	−0.3	−0.2	−1.3	−1.3	0.0	−1.1	−1.4	0.5	−0.4	−1.0	0.2
CN	−0.8	0.7	1.2	−0.7	2.3	−0.2	−0.5	0.9	−1.2	−1.5	0.2	−1.6
COOH	−0.4	0.6	1.2	0.2	2.5	−0.1	0.0	1.4	−1.1	−1.2	0.7	−1.3
NO_2	−0.9	0.9	1.4	−0.6	3.2	−0.9	−0.5	1.3	−2.8	−1.7	0.5	−2.9
ρ^{+b}	−0.6	0.8	0.3	0.1	2.9	−1.7	0.0	1.8	−3.9	−1.6	0.5	−3.3
r^c	0.90	0.95	0.40	0.10	0.94	0.94	0.10	0.93	0.98	0.98	0.63	0.99

[a] The ground effect is defined as the enthalpy of the following reaction at 298 K, X−C_6H_4−Y−Z + C_6H_6 → X−C_6H_5 + C_6H_5−Y−Z (Z = NO or H). The radical effect is defined as the enthalpy of the following reaction at 298 K, X−C_6H_4−$Y^\bullet$ + C_6H_6 → X−C_6H_5 + C_6H_5−$Y^\bullet$. [b] The slope of the correlation between BDEs and the substituent σ_p^+ constants. [c] The correlation coefficient of the correlation between BDEs and the substituent σ_p^+ constants.

BDEs equal to the difference between the ground effects and radical effects.

The results for the ground and radical effects are shown in Table 6. According to the table, separation of CH_2NO from X has a ρ^+ value of -0.6 kcal/mol ($r = 0.90$). Therefore, the electron-donating substituents disfavor the separation, whereas the electron-withdrawing substituents favor it. On the other hand, separation of CH_2-H from X has a ρ^+ value of $+0.8$ kcal/mol ($r = 0.95$). Therefore, the electron-withdrawing substituents disfavor this separation, whereas the electron-donating substituents favor it. Presumably, these behaviors relate to the electronic demands of the CH_2-H and CH_2-NO groups; that is, the CH_2NO is more electron-withdrawing than CH_2H.

Therefore, the different substituent effects on the C−NO BDEs and C−H BDEs (i.e., a difference of 1.0−1.3 kcal/mol in ρ^+) is caused by the different grounds effects, whose ρ^+ values are differed by 1.4 kcal/mol. The same explanation can be used for the nitrogen, oxygen, and sulfur cases.

Comparing the ρ^+ values in Table 7, one may find that the order of the electron withdrawing ability decrease in $O^\bullet$ (−3.9) > $S^\bullet$ (−3.3) > $NH^\bullet$ (−1.7) > S−NO (−1.6) > CH_2NO (−0.6) > O−NO (0.0) > NH−NO (0.1) > $CH_2^\bullet$ (0.3) > S−H (0.5) > CH_2-H (0.8) > O−H (1.8) > NH−H (2.9). Thus, the most significant substituent effects can be observed for the O−H → $O^\bullet$ transformation, because the change of the electron demand is very large. Indeed, ρ^+ for O−H BDE is the largest, 4.1−5.7 kcal/mol. On the other hand, very small substituent effects should be observed for the $CH_2-H \rightarrow CH_2^\bullet$ transformation, because the change of the electron demand is tiny. Indeed, the ρ^+ value for C−H BDE is very low, 0.4−0.6 kcal/mol. The only negative ρ^+ value is seen for the $CH_2-NO \rightarrow CH_2^\bullet$ transformation, because CH_2-NO is more electron withdrawing than $CH_2^\bullet$.

4. Conclusion

In the study, we used high-level theoretical methods to study the structures and bond dissociation energies of a number of X−Y−NO molecules. The main findings are as follows:

1. The syn conformation is favored by CH_3-Y-NO, C_2H_5-Y-NO, and $CH_3O-Y-NO$ (Y = C, N, O, S). The anti conformation is favored by $CH_3CO-Y-NO$ and Ph-Y−NO (Y = C, N, O). For Ph−S−NO, the syn conformation is favored because of the long S−N bond.

2. When X is an alkyl substituent, the Y−NO BDEs increase in the order X−S−NO (∼30 kcal/mol) < $X-CH_2-NO$ (∼40 kcal/mol) < X−O−NO (∼43 kcal/mol) < X−NH−NO (48 kcal/mol). When X is an aromatic substituent, the Y−NO BDEs increase in the order X−O−NO (∼21 kcal/mol) < X−S−NO (26 kcal/mol) < $X-CH_2-NO$ (∼30 kcal/mol) < X−NH−NO (∼35 kcal/mol).

3. The solvent effects of acetonitrile on the free energy change of C−NO and N−NO homolysis are significant, which are about 3−5 kcal/mol. The solvent effects of acetonitrile on the free energy change of O−NO and S−NO homolysis are relatively small, which are about 1−2 kcal/mol.

4. The remote substituent effects on C−NO, N−NO, O−NO, and S−NO BDEs have ρ^+ values of −0.4∼-0.9, 1.7−1.8, 3.2−3.9, and 1.2−1.7 kcal/mol. These values are significantly different from those on the C−H (0.4−0.6 kcal/mol), N−H (3.4−4.6 kcal/mol), O−H (4.1−5.7 kcal/mol), and S−H (2.0−3.8 kcal/mol) BDEs. Therefore, the ground effects are important for the net substituent effects on BDEs.

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References and Notes

(1) (a) Bulter, A. R.; Williams, D. L. H. *Chem. Soc. Rev.* **1993**, *22*, 233. (b) Richter-Addo, G. B.; Legzdins, P.; Burstyn, J. *Chem. Rev.* **2002**, *102*, 857.

(2) (a) Wang, P. G.; Xian, M.; Tang, X.; Wu, X.; Wen, Z.; Cai, T.; Janczuk, A. J. *Chem. Rev.* **2002**, *102*, 1091. (b) Wang, K.; Zhang, W.; Hou, Y.-C.; Xian, M.; Chen, X.-C.; Cheng, J.-P.; Wang, P. G. *Curr. Med. Chem.* **2000**, *7*, 821.

(3) Bartberger, M. D.; Mannion, J. D.; Powell, S. C.; Stamler, J. S.; Houk, K. N.; Toone, E. J. *J. Am. Chem. Soc.* **2001**, *123*, 8868.

(4) Grossi, L.; Montevecchi, P. C. *Chem. Eur. J.* **2002**, *8*, 380.

(5) (a) Cheng, J.-P.; Xian, M.; Wang, K.; Zhu, X.; Yin, Z.; Wang, P. G. *J. Am. Chem. Soc.* **1998**, *120*, 10266. (b) Zhu, X.-Q.; Xian, M.; Wang, K.; Cheng, J.-P. *J. Org. Chem.* **1999**, *64*, 4187. (c) Xian, M.; Zhu, X.-Q.; Lu, J.; Wen, Z.; Cheng, J.-P. *Org. Lett.* **2000**, *2*, 265. (d) Zhu, X.-Q.; He, J.-Q.; Li, Q.; Xian, M.; Lu, J.; Cheng, J.-P. *J. Org. Chem.* **2000**, *65*, 6729. (e) Lu, J. M.; Zhu, Q. X.; Li, Q.; He, J. Q.; Xian, M.; Cheng, J. P. *Chem. J. Chin. University* **2000**, *21*, 570. (e) Lu, J.-M.; Wittbrodt, J. M.; Wang, K.; Zhong, W.; Schlegel, H. B.; Wang, P. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **2001**, *123*, 2903.

(6) (a) Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342. (b) dos Santos, R. M. B.; Muralha, V. S. F.; Correia, C. F.; Simoes, J. A. M. *J. Am. Chem. Soc.* **2001**, *123*, 12670.

(7) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) (a) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327. (b) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210. (c) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *1F06*, 5151.

(10) Muller, R. P.; Nonella, M.; Russegger, P.; Huber, J. R. *Chem. Phys.* **1984**, *87*, 351.

(11) Bartberger, M. D.; Houk, K. N.; Powell, S. C.; Mannion, J. D.; Lo, K. Y.; Stamler, J. S.; Toone, E. J. *J. Am. Chem. Soc.* **2000**, *122*, 5889.

(12) The role of hyperconjugation in the conformation equilibrium of nitroso compounds was mentioned in an earlier study: Brown, H. W.; Hollis, D. P. *J. Mol. Spectrosc.* **1964**, *13*, 305. However, detailed explanation may not be that simple. A balance between repulsion and different hyperconjugation interactions has to be taken into consideration.

(13) Itoh, M.; Takenaka, K.; Okazaki, R.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2001**, 1206.

(14) Cox, A. P.; Hardy, J. A.; Randell, J. *J. Mol. Struct.* **1995**, *352/353*, 299.

(15) Cox, A. P.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5071.

(16) Turner, P. H.; Corkill, M. J.; Cox, A. P. *J. Phys. Chem.* **1979**, *83*, 1473.

(17) Song, K.-S.; Cheng, Y.-H.; Fu, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *J. Phys. Chem. A* **2002**, *106*, 6651.

(18) Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2305.

(19) *CRC Handbook of Chemistry and Physics*, 81st ed.; Lide, D. R., Ed.; CRC Press LLC: Boca Raton, FL, 2000.

(20) (a) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877. (b) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518.