On the Stabilisation of a Singlet Nitrene by the Phosphaniminato and Related Imine-Type Substituents, a Quantum Chemical Investigation

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Dedicated to Prof. K. Dehniche on the occasion of his 70th birthday

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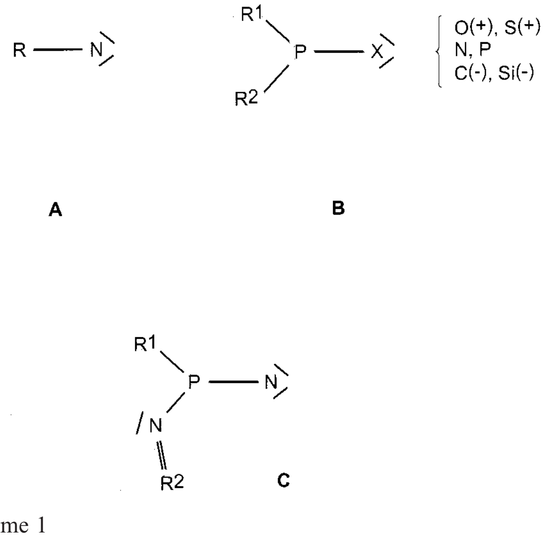
The substituent effects on the singlet–triplet energy separations are explored for phosphanylnitrenes and related congeners from the Group 14 to Group 16 elements. Imine-type substituents (e.g. phosphaniminato, methyleneimine etc.) are more effective than amino groups in lowering the energy of a singlet below that of a triplet state. It is due to an effective stabilisation of the singlet and a destabilisation of the triplet.

Introduction

Nitrenes **A** are highly unstable species.[1−3] They become more stable in the case of phosphanylnitrenes **B** (X = N) that are substituted with bulky amino groups at the phosphorus atom (R^1,R^2 = NR'_2, R′= alkyl) (Scheme 1). It opens a wide field for the syntheses of new types of structures in low-coordination phosphorus chemistry.[4−9] Similarly, amino-substituted phosphanylphosphinidenes are considered as useful intermediates.[10−12] Consequently, the particular role of the amino group as a stabilising factor on a singlet ground state of a nitrene has been addressed by a variety of quantum chemical investigations.[13−21]



Scheme 1

These investigations indicate that nitrenes and especially phosphinidenes possess small energy separations between the singlet and the lowest-energy triplet state. On this basis, nitrenes are reminiscent of carbenes[22] as was recently summarised.[23,24]

Despite the wealth of investigations into nitrenes, important aspects that have hitherto not been investigated remain open: (1) The electronic structures of valence isoelectronic nitrene homologues of type **B**, with X originating from Group 16 (X = $O^{(+)}$, $S^{(+)}$) or from Group 14 (X = $C^{(-)}$, $Si^{(-)}$). In the present quantum chemical study, it will be shown that the Group 16 homologues possess singlet ground states and that the Group 14 homologues possess triplet ground states. (2) The effect of an imino function of type **C** in which a lone-pair is adjacent to the phosphorus atom. Evidence is given that these types of substituents [R^2= PH_3, $C(NH_2)_2$, CH_2, PH] are essentially more effective than amino groups in moving the energy of the singlet below that of the triplet, thus making it the ground state. A peculiar π-donating effect of methyleneimine-substituted iminophosphanes has been found.[25,26] The status of oxo- and thioxophosphonium ions has also been summarised recently.[6] The details of the calculations are given in the Theoretical Section at the end of this publication.

Results and Discussion

a. Qualitative Considerations

According to EH calculations,[27] the relevant molecular-orbital system of the parent phosphanylnitrene (C_{2v} symmetry imposed) is as follows (Figure 1).

The frontier orbitals are the p-orbital of the nitrogen atom (HOMO), in plane with the residual atoms, and the π* molecular orbital (LUMO) of the P−N bond. Phosphorus is much less electronegative than nitrogen,[28] hence the larger coefficient in the π* molecular orbital is at the phosphorus atom. In the π molecular orbital (HOMO-1), the opposite is true: the larger coefficient is located at the more electronegative nitrogen atom.

The two relevant lowest-energy electronic states (singlet and triplet) are constructed from these orbitals. The re-

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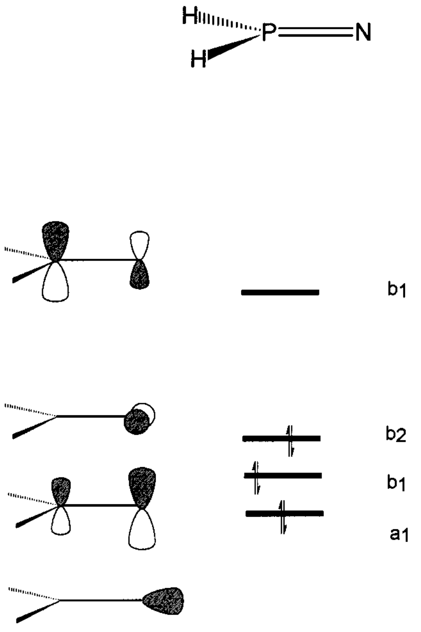


Figure 1. Frontier orbital system of the parent phosphanylnitrene

sulting Slater determinants for these states (C_{2v} symmetry) are as follows:

Ψ ($^1A_1$) = ...$(a_1)^2(b_1)^2(b_2)^2$>

Ψ ($^3A_2$) = ...$(a_1)^2(b_1)^2(b_2)^1(b_1)^1$>

MCSCF calculations[29] on the parent phosphanyl nitrene indicate that the given Slater determinants describe both states well. Geometry optimisation results in a planar structure (C_{2v} symmetry) for the singlet, while the triplet adopts a pyramidal structure at the phosphorus atom (C_s symmetry). The equilibrium structures are illustrated in Molden plots[30] shown in Figure 2 for the equilibrium singlet (top) and triplet (bottom) structures. The findings agree with the previous considerations of phosphanyl nitrenes.[14]

From the one-electron considerations, the following tendencies of the stabilities of the nitrenes and their valence isoelectronic homologues are observed: (a) π-Donating substituents raise the energy of the LUMO (π*), owing to conjugation with this molecular orbital. The HOMO (p) is generally not affected by substituents at the phosphorus atom. Consequently, π-donating substituents increase the energy difference between the HOMO and the LUMO, and a singlet ground state is pronounced. (b) On the other hand, π-electron-attracting substituents favour a triplet ground state. The ability to enhance a singlet ground state should become more pronounced with increasing polarity of the P−X π-bond, i.e., in the order X = $O^{(+)} > N > C^{(-)}$. (c) When the terminal main group element X is less electronegative, the energy of the HOMO raises stronger than the energy of the LUMO. In other words the energy gap between these orbitals decreases and a triplet ground state is facilitated. It corresponds to the hypothesis that a singlet ground state is expected for these species in the order X = $C^{(-)} < N < O^{(+)}$. As will be shown below, a further effect is important for the strength of the resulting P−N π-bond in the singlet state of the nitrene. Strong σ-electron-withdrawing substituents at the phosphorus atom strengthen the P−N bond.

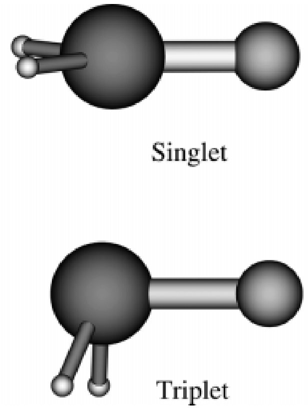


Figure 2. Molden plots of equilibrium singlet ($^1A_1$, C_{2v} symmetry) and triplet states ($^3A''$, C_s symmetry) of the parent phosphanylnitrene

b. Phosphanylnitrene and Substituent Effects

We first investigated the parent systems, i.e., the phosphanylnitrene and its related valence isoelectronic homologues. The corresponding Group 14 and Group 16 congeners of various elements X were considered. The most relevant bonding parameters for the investigated species in their lowest-energy singlet and triplet states are collected in Table 1. The various electronic states were evaluated at the density functional level [B3LYP/6-31+g(d)] and at the more sophisticated CCSD(t) level. For the latter, a valence triple-zeta basis set augmented by diffuse functions was used. The more elaborate CCSD(t) calculations parallel the trends already observed at the density functional level. However, in general they tend to enhance more the stabilities of the singlet species. In the case of the nitrenes, the results also agree

Table 1. Relevant bonding parameters (bond lengths in Å, bond angles in degrees) and singlet−triplet energy differences (in kcal/mol) of phosphanylnitrenes and element homologues H_2PX; the first entry is the singlet ($^1A_1$, C_{2v} symmetry), the second entry is the triplet ($^3A''$, C_s symmetry), electron affinities and/or ionisation potentials (in eV) are given in parentheses

X	P−X	XPH	HPH	Δ*E* (DFT)[a]	Δ*E* [CCSD(t)][b]
$C^{(-)}$	1.646	131.8	96.3	−0.3 [1.2][c]	0.0
	1.833	128.0	104.0	0.0	1.8
$Si^{(-)}$	2.125	131.7	96.7	−6.8 [0.9][c]	−7.0
	2.393	102.8	92.4	0.0	0.0
N	1.522	127.6	104.9	0.0 [9.4;1.3][d]	0.0
	1.718	98.9	95.9	6.9	13.3
P	1.962	128.3	103.3	0.0 [8.1;1.6][d]	0.0
	2.209	98.7	94.6	−2.4	−0.3
$O^{(+)}$	1.462	122.1	115.9	0.0 [9.1][e]	0.0
	1.609	102.5	109.1	39.8	49.9
$S^{(+)}$	1.822	123.9	112.2	0.0 [8.7][e]	0.0
	2.070	102.7	103.7	18.3	25.5

[a] B3LYP/6-31+g(d) plus zero-point vibrational energy (*ZPE*) correction. − [b] CCSD(t)/aug-cc-pVTZ//B3LYP/6-31+g(d). − [c] Ionisation potentials (in eV) for the formation of the corresponding cation doublet states, with *ZPE* correction. − [d] The first entry is the ionisation potential, the second entry is the electron affinities. − [e] Electron affinities (in eV) towards anion doublets, with *ZPE* correction.

with the quantum chemical investigations already presented (see ref.[21] and cited work).

On the contrary, the species with X = $C^{(-)}$ or $Si^{(-)}$ are most likely to be found in a triplet ground state. At the very least, the singlet−triplet energy separations are fairly small. When X is more electronegative than nitrogen, a strong preference for a singlet ground state is observed. One may of course question whether the carbide or silicide analogues may exist at all, in the sense that in the corresponding singlet state, the negative charge will be kept in the structure or it undergoes spontaneous ionisation with the loss of an electron. In order to obtain a deeper insight into this aspect, we have also examined the corresponding lowest-energy doublet states ($^2B_2$, C_{2v} symmetry). The corresponding energy quantities (energy values obtained at the density functional level, in eV) are shown in the table in parentheses. Accordingly, the corresponding radicals have only a small tendency to add a further electron in the formation of a carbide or a silicide, but alternatively a rather large electron affinity is obtained for the Group 15 and Group 16 congeners.

Next we studied the effect of a typical π-donor (R^1, R^2 = NH_2) or π-acceptor (SiH_3) on the phosphanylnitrene and its valence isoelectronic homologues. The results of these investigations are collected in Table 2. Since the more elaborate CCSD(t) calculations parallel those at the density functional level, the following discussion will be based on the results calculated at the density functional level.

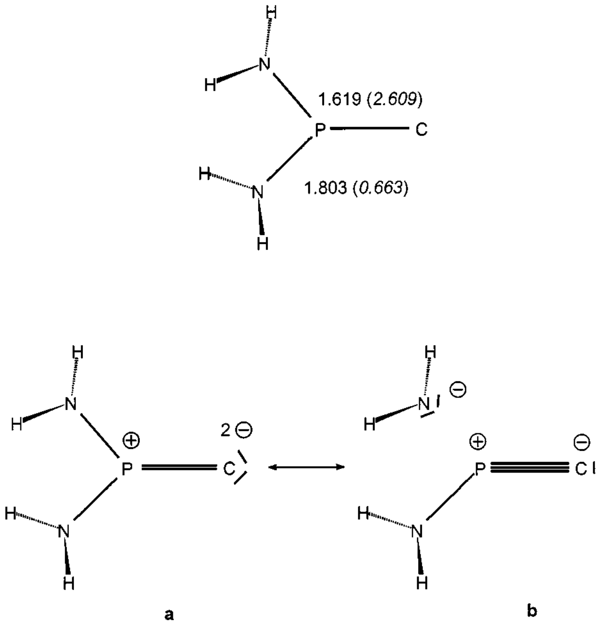
In accordance with the qualitative considerations, amino groups at the phosphorus atom tend to stabilise a singlet rather than a triplet ground state. Silyl groups do the opposite. The π-donation is most effective for the Group 16 congeners (X = $O^{(+)} > S^{(+)}$) and least effective for X = $C^{(-)}$ and $Si^{(-)}$. For the latter species the ground state is a triplet.

In all cases, the resulting P−X bonds are shorter than those of corresponding double bond systems, for example, in iminophosphanes (ca. 1.54 Å)[31] or methylenephosphanes (ca. 1.64 Å).[32,33] Simultaneously, the bonds towards the trigonal phosphorus atom are significantly elongated. The most striking example is the diaminophosphanyl carbide, in which the P−N bonds become 1.803 Å, which is longer than a P−N single bond (1.76 Å).[28] An NBO population analysis[34] (Wiberg bond orders in italics) gives the results shown in Scheme 2.

Table 2. Substituent effects on the singlet−triplet energy separations (in kcal/mol) in nitrene homologues R^1R^2PX, at the B3LYP/6-31+g(d) level

R^1	R^2	X	Symmetry[a]	P−N [Å][a]	Δ*E* [kcal/mol]
NH_2	NH_2	$C^{(-)}$	C_2	1.619	0.7
SiH_3	SiH_3	$C^{(-)}$	C_1	1.660	−2.6
NH_2	NH_2	$Si^{(-)}$	C_2	2.065	−4.4
SiH_3	SiH_3	$Si^{(-)}$	C_1	2.148	−8.1
NH_2	NH_2	N	C_2	1.504	21.8
SiH_3	SiH_3	N	C_1	1.542	5.1
NH_2	NH_2	P	C_2	1.934	9.5
SiH_3	SiH_3	P	C_1	1.996	−2.0
NH_2	NH_2	$O^{(+)}$	C_2	1.459	55.0
SiH_3	SiH_3	$O^{(+)}$	C_1	1.489	28.5
NH_2	NH_2	$S^{(+)}$	C_2	1.879	37.1
SiH_3	SiH_3	$S^{(+)}$	C_1	1.923	17.9

[a] Singlet states.



Scheme 2

The weakening of the P−N (amino) bonds is compensated by the strengthening of the P−C bond. It can be attributed to the participation of the limiting structures **b** versus **a**, because the negative charge is shifted from the less electronegative carbon atom to the more electronegative nitrogen atoms.

We have also probed the effect of push-pull substitution at the phosphorus atom, i.e., R^1 = NH_2, R^2 = SiH_3. The effect on the singlet−triplet energy separation (17.4 kcal/mol) is similar to the effect of the monoamino-substituted nitrene (17.5 kcal/mol). In addition, we have investigated the case where the two amino groups are incorporated into a five-membered ring system *cyclo*-[N(H)CH=CHN(H)PN]. The singlet−triplet energy separation (18.0 kcal/mol) is similar to that found with monoamino substitution, but less than with diamino substitution (21.8 kcal/mol).

c. Amine- versus Imine-Type Substituents

A significant shortening of the P−X bond is observed for the nitrenes (X = N), in cases where strongly electronegative substituents are attached to the phosphorus atom

Table 3. Singlet−triplet energy separations (in kcal/mol) in various substituted nitrenes R^1R^2PN, at the B3LYP/6-31+g(d) level

R^1	R^2	Symmetry[a]	P−N [Å][a]	ΔE [kcal/mol]
NH_2	H	C_2	1.508	17.5
SiH_3	NH_2	C_1	1.517	17.4
F	H	C_s	1.499	18.2
F	F	C_{2v}	1.495	3.4
OH (*E*)	H	C_s	1.504	21.6
cyclo-[N(H)CH=CHN(H)]		C_2	1.508	18.0
H_3PN (*Z*)	H	C_1	1.516	24.8
H_3PN (*Z*)	H_3PN (*Z*)	C_1	1.523	32.6
H_3PP (*Z*)	H	C_1	1.531	18.1
H_2CN (*Z*)	H	C_1	1.517	15.2
$(H_2N)CN$ (*Z*)	H	C_1	1.521	25.5
HPN (*Z*)	H	C_1	1.520	15.5

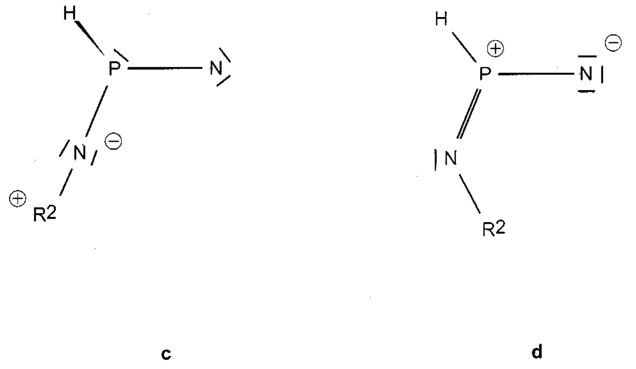
[a] Singlet states.

(Table 3), for R^1, R^2 = F or OH. These substituents are capable of polarising the phosphorus atom, i.e., to withdraw p-electron density from it. As a consequence, the σ-bond of P−N experiences more s-character and is shortened. In essence, it increases the stability of the P−N multiple bond.

At first glance, one would expect an increased singlet−triplet energy separation. However, electronegative substituents at the phosphorus atom have another effect, too. It is known that electronegative substituents increase the inversion barrier at a phosphane group.[35,36] Thus, electronegative substituents also favour a pyramidal triplet state. The calculated data (see Table 3) confirm this assertion. Fluorine, which is a poor π-donor but a strong electron-withdrawing σ-acceptor, tends to shorten the P−N bond (relative to the parent phosphanylnitrene). One fluorine atom (R^1/R^2 = F/H) shortens the P−N bond and increases the singlet-triplet energy separation, but the introduction of a second fluorine atom (R^1/R^2 = F/F) further reduces the P−N distance and simultaneously decreases the singlet−triplet energy difference. The special effect of fluorine substitution on the P−N bond length in the phosphanylnitrene is in agreement with the analogous limiting structure **a** and **b**, as has previously been noted[21].

The amino group is a strong π-donor (p-orbital) but on the other hand is also a strong σ-acceptor (sp^2-orbital). It is thus not the most suitable substituent for singlet stabilisation. A more appropriate substituent for singlet stabilisation should be a stronger π-donor as well as weaker σ-acceptor than the amino group. The latter aspect is of importance, otherwise the pyramidal triplet is equally well stabilised. A substituent that is more suitable for this purpose was therefore sought.

It has been well established that a phosphaniminato ligand can coordinate to a transition-metal fragment with a strong variation of the valence angle at the nitrogen atom.[37] More generally, it indicates that an imino function exerts σ-effects which are *dynamically* operative. This means that the σ-inductive effect of the same substituent can act differently in the lowest-energy singlet or triplet state. The two extreme bonding features (Scheme 3), **c** versus **d** are considered.



Scheme 3

In **c**, the nitrogen atom is sp-hybridised, while in the bent structure **d** it is sp^2-hybridised (PNP = 120°) [or sp^3 (109°)]. In **c** two lone pairs at the imino nitrogen atom are present, thus destabilising the triplet (with a pyramidal phosphorus atom, see Figure 2) by lone-pair repulsion (N vs. P). On the other hand, π-conjugation of the imino nitrogen atom with the phosphorus atom is present in **d**, and a singlet ground state is favoured. It should be noted that in the case of an amino group, lone-pair repulsion can be avoided in the triplet state by rotation of the amino group. Based on the present considerations, one can predict that substituents at the phosphorus atom that have an imino rather than an amino functional group are more likely to stabilise singlet ground states in the nitrenes and related species.

In order to strengthen these arguments, quantum chemical calculations [at the B3LYP/6-31+g(d) level] were performed on a variety of substituents with imino functions in the α-position to the phosphorus atom, namely, the phosphaniminato ($H_3P{-}N$), phosphanephosphinato ($H_3P{-}P$), methyleneimino ($H_2C{-}N$), diamino(methyleneimino) [$(H_2N)_2C{-}N$], and iminophosphane (HP=N) substituents (Table 3). Corresponding Molden plots of the equilibrium lowest-energy singlet and triplet states are shown representatively for the phosphaniminato ligand in Figure 3.

The structures preferentially adopt (*Z*) conformations. The P−N multiple bonds are significantly longer than in

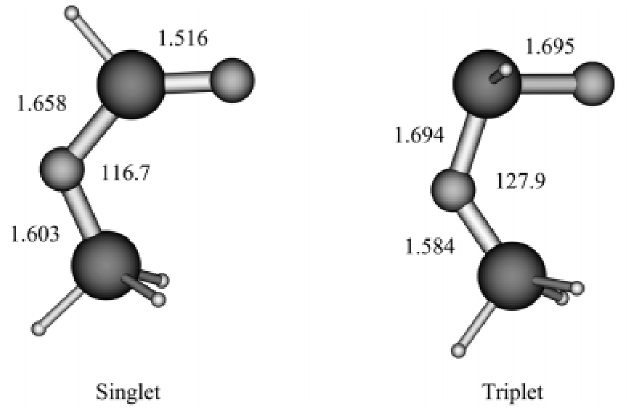
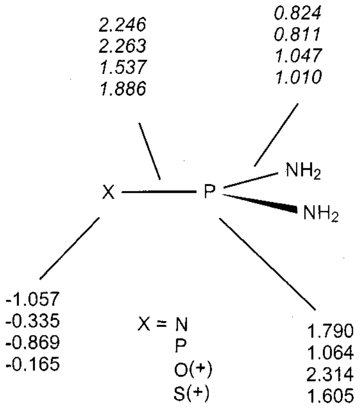


Figure 3. Molden plots of monosubstituted phosphaniminatonitrene; singlet state (left), lowest-energy triplet state (right)



Scheme 4

the amino-substituted nitrenes (see Table 2), and the singlet−triplet separations are enlarged. Similar trends, shown here only for the phosphaniminato ligand, were observed for the other imino-type substituents, type **C**. For the phosphaniminato ligand we have also probed the case of disubstitution. The trend in mono- vs. disubstitution is not additive. It is worth noting the peculiar role of the phosphaniminato ligand which has also recently been shown to stabilise the singlet of phosphanylcarbenes.[38] Imine-type functional groups are also predicted to lengthen the strained P−P bond in 1,2-diphosphacyclobutene.[39]

Based on the singlet−triplet energy separations (see Table 1) the diamino-substituted oxo- and thioxophosphonium species should be fairly stable. In their planar singlets, the central phosphorus atom is surrounded by electronegative substituents. Results from the NBO population analysis for the case of **B** (R^1 = R^2 = NH_2 and X = , N, P, $O^{(+)}$, $S^{(+)}$) are shown in Scheme 4 (Wiberg bond orders are italicised).

The central atom (P) gains a large positive charge in the cations since the electron density is withdrawn to the peripheral atoms which are more electronegative than the central phosphorus atom. It is known that the thioxophosphonium cations and the nitrenes spontaneously dimerise to form four-membered ring systems.[6]

Conclusion

The results of our investigations can be summarised as follows:

(1) Singlet nitrenes are stabilised by π-donors. The stabilisation effects increase for the Group 16 and decrease for the Group 14 congeners. The opposite is true for π-attracting substituents. The carbides and silicides possess triplet ground states.

(2) Substituents which bear an imino function in an α-position to the phosphorus atom, e.g., the phosphaniminato ligand, promote a singlet ground state even more strongly than an amino group. Our investigations have thus revealed a new type of substituent for the stabilisation of species which were hitherto considered as being short-lived intermediates. In the experiment, however, the structures are encumbered by bulky substituent effects which in addition affect the kinetic stabilities of these species.

Theoretical Section

All calculations were performed with the Gaussian-98 set of programs.[40] The various structures were fully optimised at the B3LYP level by using the 6-31+g(d) basis set.[41−43] The density functional is built with Becke's three-parameter exchange functional[44,45] and the nonlocal correlation functional of Lee, Yang, and Parr.[46] The energy optimisations were conducted by analytically determined nuclear coordinate gradients. All the investigated structures were characterised by vibrational analysis within the harmonic approximation. The population analysis at the given optimised geometries were carried out according to the Weinhold−Reed partitioning scheme.[34] Further correlation corrections were obtained at the CCSD(t) level[47−49] by using triple-zeta valence basis sets[50,51] augmented with diffuse functions. One may note that the singlet−triplet energy separations within density functional theory depend on the shape of the chosen functional.[52] Nevertheless, the chosen density functional method is expected to predict correct trends for the substituent effects.

Acknowledgments

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