Table II. Relative Energies (kcal/mol) of Potential Diradical and Perepoxide[a] Intermediates in Reactions of Singlet Oxygen with Electron-Rich Alkenes, According to UM3 Calculations

		$\sigma\pi$			$\pi\pi$	
alkene	intermediate	anti	syn		anti	syn
propene	**6a**	0.0[b]	0.7		−0.4	0.7
	7a	10.1			9.9	
	perepoxide			8.6		
2-methylpropene	**6b**	0.0[c]	1.0		0.9	3.8
	7b	19.9			19.8	
	perepoxide			13.3		
2-methoxypropene	**6c**	0.0[d]	1.0		3.2	5.7
	7c	22.9			22.9	
	perepoxide			2.13		
2-methyl-2-butene	8a	0.0[e]	1.2		0.9	
	9a	9.7			8.8	
	perepoxide			7.2		
2-methoxy-2-butene	8b	0.0[f]			5.7	
	9b	12.7			13.3	
	perepoxide			13.8		
methoxyethylene	**10**	0.0[g]	1.0		3.6	8.2
	11	14.9			15.1	
	perepoxide			16.6		

[a] The exocyclic oxygen is syn to the methyl or methoxy groups. [b] −1088.339 eV. [c] −1245.056 eV. [d] −1556.450 eV. [e] −1401.637 eV. [f] −1713.094 eV. [g] −1299.555 eV.

derivatives. The syn and anti forms of the $\sigma\pi$ diradical are eclipsed and staggered about the C–O single bond as illustrated in Scheme II. The former corresponds to the local maximum on the potential surface for the internal rotation of the O_2 group around the C–O bond. The relative energies given in Table II demonstrate the 0.7–3.1 preference of the anti (staggered) over the syn (eclipsed) geometries. Thus, it is unreasonable to assume that the syn $\sigma\pi$ diradical is a plausible intermediate in ene reactions.[8] On the other hand, the anti $\sigma\pi$ diradical might be a true intermediate for the reactions. However, if so, the internal rotations of alkyl and alkoxy groups should be facile, since the bonding interactions between the 1,4-diradical sites are negligible. In order to confirm this point we have performed full geometry optimizations on the $\pi\pi$ diradicals, **2R**-$\pi\pi$, and substituted derivatives. The energy differences between the anti $\sigma\pi$ and $\pi\pi$ diradicals are very small, indicating essentially free rotation of these groups. The situation is similar even for the syn conformers. This implies that the ene reaction between singlet oxygen and a suitable substituted alkene or enol ether would be nonstereospecific if the diradical were an intermediate in these reactions. As mentioned previously,[1,10] stereospecificity has been observed experimentally.

The geometries of the terminal carbon radical centers of the $\sigma\pi$ and $\pi\pi$ diradicals are found to be similar to those of corresponding alkyl and alkoxy free radicals, which are known to have very small rotational barriers.[17] The C–O and O–O bond lengths are essentially identical with the corresponding optimized bond lengths of peroxide radicals. Thus the 1,4-diradicals examined here may be regarded simply as the coupled states of two free radicals. The optimized geometries of the diradicals, **7c**, **8b**, and **11**, formed by α attack on enol ethers exhibit a characteristic conformation of the O_2 group with respect to the MeO. Similar conformations are observed for ethanediol-like species. This conformation is characteristic of an "anomeric effect" stabilization.[4,8] In spite of such stabilization, however, the relative stabilities of the diradicals are normal; the more substituted radical is more stable. Thus it seems difficult to regard the anomeric effect as a determining factor of the anti-Markovnikov-type regioselectivities observed for ene reactions, although it plays an important role for conformational stabilizations of methanediol species.

Although both the UM3 and U3G, and GVB calculations predict the greater stability of the $\sigma\pi$ diradical intermediate than the perepoxide intermediate in the case of alkenes and enol ethers, as shown in Tables I and II, they do not prove that ene reactions of these species proceed through a diradical mechanism.[4,8] Indeed, theoretical results described here and experimental results are not compatible with the diradical mechanism.[1,5,10] Although our theoretical evidence is circumstantial rather than direct, we feel that these results exclude all but concerted mechanisms, with simultaneous CO and OH bond making.

Acknowledgment. The ab initio HF (STO-3G) calculations were carried out at the Institute for Molecular Science (Okazaki, Japan). The author (K.Y.) thanks Professor K. Morokuma and Dr. S. Kato for their discussions. Financial support of this research from the National Science Foundation (to KNH) is gratefully acknowledged.

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(18) (a) Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1. (b) Foote, C. S. *Pure Appl. Chem.* **1972**, *27*, 635.

(19) Singlet molecular oxygen ($^1O_2$) may simultaneously attack the π bond and the allylic hydrogen in the initial stage of ene reactions as shown in a previous paper: Yamaguchi, K. *Jpn. Chem. Rev.* **1973**, *1*, 292. This model emphasizes the importance of the attack of the C–C double bond instead of the terminal carbon atom as in the case of perepoxide model, but it requires participation of allyl hydrogen for maximizing the allowed orbital interactions.

The Origin of the Pyramidalization of the *tert*-Butyl Radical

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Received November 7, 1980

Abstract: The pyramidal nature of the *tert*-butyl radical is confirmed by ab initio UHF calculations with the 4-31G basis set. Each CH_3–C· bond is predicted to be 22.1° out of the plane of the ·$C(CH_3)_2$ group. The calculated barrier to inversion is 1.2 kcal/mol. The transition state for inversion has C_{3h} symmetry, while the energy minimum has C_{3v} symmetry, so that methyl rotation is synchronized with inversion. The pyramidalization of *tert*-butyl simultaneously maximizes hyperconjugative stabilization of the radical, and minimizes torsional interactions between the methyl groups and the radical center.

The geometry of the *tert*-butyl radical has been a matter of considerable dispute during the last decade. Prior to 1972, this species was generally conceded to have a planar carbon skeleton with a low out-of-plane bending force constant, much like the

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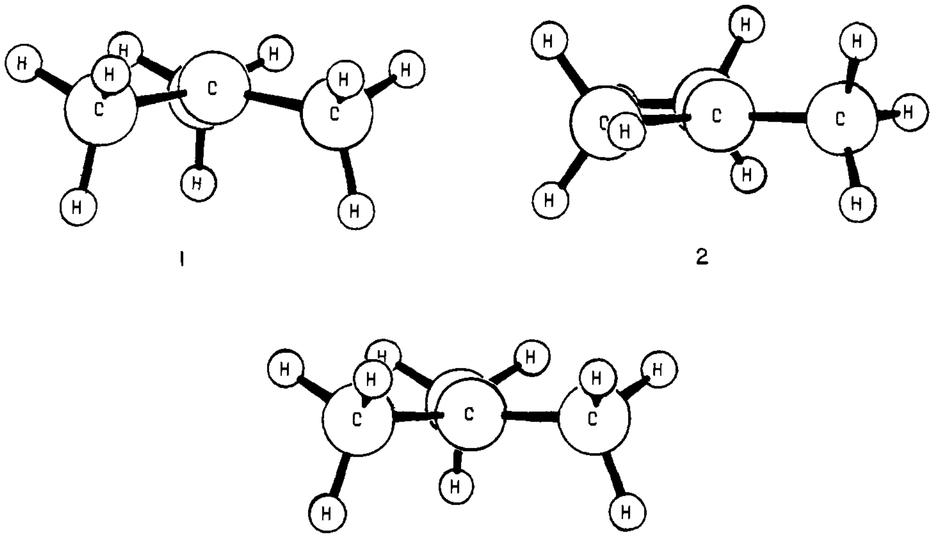
Chart I



1 2 3

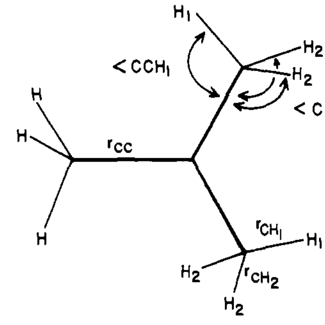
methyl radical.[2] In 1972, Wood, Williams, Sprecher, and Lathan measured the magnitude and temperature dependence of the ^{13}C hfs in the ESR spectrum, and performed ab initio STO-3G calculations on *tert*-butyl; they concluded that the *tert*-butyl radical is significantly pyramidal.[3] This conclusion has been disputed on both experimental and theoretical grounds.[5,6] In cases where definite experimental evidence for nonplanarity has been obtained, the possibility of solvent-induced pyramidalization has been raised.[6]

We have computed the structure of the *tert*-butyl radical at a theoretical level (ab initio UHF calculations with the 4-31G basis set),[7] which has been shown to give reasonable geometries and force constants for smaller radicals.[8] We also propose an explanation for the pyramidalization of *tert*-butyl and all alkyl radicals other than the methyl radical. This explanation is supported by calculations on *tert*-butyl and by the detailed theoretical studies of the isopropyl radical reported during the course of this work by Pacansky and Dupuis.[8d,e]

Results

The three conformations central to our arguments are shown in Chart I,[9] and the geometries and energies are summarized in Table I. According to the UHF 4-31G calculations, the energy minimum for the *tert*-butyl radical is **1**, in which each CC bond is bent out of the plane defined by the central carbon and the other two methyl carbons by $\theta_b = 22.1°$. This corresponds to a structure

Table I. Predicted Geometries and Energies of the *tert*-Butyl Radical in Three Geometries by 4-31G Calculations (STO-3G Values in Parentheses)[a, b]



	conformation		
	1	2	3
	C_{3v} (pyramidal)[c]	C_{3h}	C_{3v} (planar)
energy, au	−156.45051 (−154.83549	−156.44855 (−154.83363)	−156.44849
E_{rel}, kcal/mol	0 (0)	1.23 (1.17)	1.27
dihedral ∠CCCH$_1$ (fixed)	90	180	90
θ_b	22.1 (24.4)	0 (0)	≡0
θ_{min}	7.4 (8.2)	0 (0)	0
r_{CC}	1.503 (1.524)	1.502 (1.521)	1.502
r_{CH_1}	1.091 (1.090)	1.083 (1.086)	1.090
r_{CH_2}	1.084 (1.086)	1.088 (1.089)	1.084
∠CCH$_1$	111.5 (111.2)	111.6 (111.0)	
∠CCH$_2$	111.4 (110.8)	111.6 (111.2)	112.4

[a] Distances in Å, angles in deg. [b] All S^2 = 0.76, indicating that spin contamination will have no significant influence on relative energies.[8] [c] This structure is similar to that obtained by using STO-3G calculations and partial geometry optimization.[3]

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(1) (a) On leave from New South Wales Institute of Technology, Sydney, Australia, 1980. (b) Address correspondence to this author at the University of Pittsburgh.

(2) Symons, M. C. R., *Nature (London)* **1969**, *224*, 686 and references therein. For the most recent infrared study of *tert*-butyl, see: Pacansky, J.; Chang, J. S. *J. Chem. Phys.* **1981**, *74*, 5539.

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(4) References on this subject are summarized in ref. 5 and 6.

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(6) Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978**, *100*, 6750.

(7) Calculations were carried out with use of the GAUSSIAN 70, 74, and 80 series of programs written by Pople and co-workers and the 4-31G split-valence (Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724) and STO-3G minimal (Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657) basis sets. We thank Professor Pople and Michael Frisch for access to and assistance with GAUSSIAN 80.

(8) (a) Pacansky, J; Dupuis, M. *J. Chem. Phys.*, **1978**, *68*, 4276. (b) Pacansky, J.; Dupuis, M. *J. Chem. Phys.* **1979**, *71*, 2095. (c) Pacansky, J.; Coufal, H. *J. Chem. Phys.* **1980**, *72*, 5285. (d) Pacansky, J.; Dupuis, M. *J. Chem. Phys.* **1980**, *73*, 1867. (e) **Note Added in Proof:** Yoshimine and Pacansky (Yoshimine, M.; Pacansky, J. *J. Chem. Phys.* **1981**, *74*, 5168) have reported independent 4-31G calculations on *tert*-butyl. These calculations agree with those reported here, and provide greater detail on other conformations.

(9) The drawings were prepared on PROPHET, a biomedical computer system sponsored by the National Institutes of Health, Division of Research Resources.

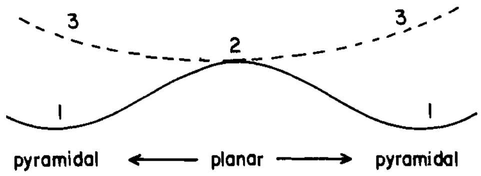
Table II. Computed Pyramidalizations and Barriers to Inversion of Alkyl Radicals

radical	computational level	out-of-plane bending angle (θ_b), deg	barrier to inversion, kcal/mol	ref
methyl	UHF//4-31G	0	0	*c*
ethyl	RHF//[8s,4p;4s]/[4s,3p;3s]	6.2[b]	0.20	8a
	UHF//[8s,4p;4s]/[4s,3p;3s]	6.1	0.06	8a,d
	UHF//[8s,4p;4s]/[4s,3p;3s] + pol		0.16	
gauche-propyl	UHF//4-31G	11.3	0.03	8b
isopropyl (4)[a]	UHF//[8s,4p;4s]/[4s,3p;3s]	5.8	0.47	8d
isopropyl (5)[a]	UHF//[8s,4p;4s]/[4s,3p;3s]	15.9	0.33	8d
tert-butyl	UHF//4-31G	22.1	1.2	this work, 8e

[a] Comparable results were found with 4-31G.[8d] [b] Optimized angles were stated to agree within 0.5° for RHF and UHF calculations. [c] Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1971, *93*, 808.

with each CC bond bent out of the plane defined by the three methyl carbons by $\theta_{min} = 7.4°$. For comparison, a perfectly "tetrahedral" radical formed by excising a hydrogen from methane would have $\theta_b = 54.8°$ and $\theta_{min} = 19.5°$; thus, the *tert*-butyl is ~40% pyramidalized to a "tetrahedral" structure. The pyramidalized structure, **1**, resembles the optimum staggered structure of isobutane, for which the angle corresponding to θ_{min} is 18.0°.[10] STO-3G calculations, which generally give larger pyramidalizations than 4-31G for closed-shell systems,[11] predict a slightly greater pyramidalization of *tert*-butyl. For the ethyl radical, 4-31G calculations give geometry and inversion barrier predictions close to more sophisticated calculations including polarization functions.[8] For that reason, we describe only the 4-31G results. Nevertheless, the similarity of the STO-3G and 4-31G results indicates that our conclusions are not an artifact of use of a particular basis set.

The lowest energy planar conformation of *tert*-butyl is **2**, which has C_{3h} symmetry and is 1.2 kcal/mol above the pyramidal structure in energy. The C_{3v} conformation with a planar heavy atom skeleton, **3**, is slightly higher in energy and collapses to **1** upon full optimization. Other reasonable conformations of *tert*-butyl are higher in energy than **1**–**3**. Thus, these calculations predict that *tert*-butyl is pyramidal, with C_{3v} symmetry, but inverts via the C_{3h} transition state, **2**, as shown by the heavy line in the diagram below:

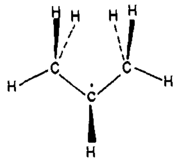


Structure **2** is *not* an energy minimum, but calculations in which methyl rotations are *not* included will produce the spurious result that *tert*-butyl is planar.[12] The 4-31G barrier to inversion (1.2 kcal/mol) is higher than that found experimentally by Griller, Ingold, and co-workers (0.45–0.51 kcal/mol)[6] in solution, but the degree of pyramidalization found by these workers ($\theta_b = 33.6°$; $\theta_{min} = 11.5°$) is somewhat larger than that computed here.[13]

Discussion

Computational studies of a varietry of simpler radicals, primarily by Pacansky and Dupuis,[8] are summarized in Table II. For ethyl, these authors showed that ROHF and UHF calculations at various levels give similar predictions as to the extents of pyramidalization of these radicals. They also found that pyramidalization increases with the number of α–methyl groups. These results, and ours for *tert*-butyl, indicate that this trend is a consequence of torsional effects combined with the unsymmetrical hyperconjugative interactions exerted by a methyl group on a radical center when one methyl CH bond eclipses the half-occupied orbital.

If the radical center of the ethyl radical is constrained to planarity, the bisected and eclipsed forms are isoenergetic. The eclipsed form has a plane of symmetry, no unsymmetrical forces, and remains planar like methyl. However, the radical center of the bisected form, **6**, experiences an unsymmetrical perturbation from the methyl group. Torsional interactions between the vicinal CH bonds should favor slight pyramidalization toward a staggered geometry about the CC bond, and this distortion also permits a small additional stabilization through an increase of the hyperconjugative interaction between the α-CH bond orbitals and the half-occupied p orbital as shown in **6**:



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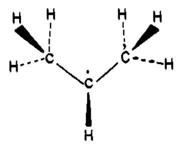
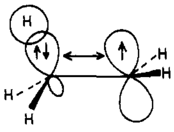


5



6

For the isopropyl radical in conformation **5**, and in the preferred conformation of the *tert*-butyl radical, **1**, both torsional effects and increased hyperconjugation are doubled and tripled, respectively, and pyramidalization increases accordingly. However, for *tert*-butyl, the lowest energy conformation is far more pyramidal ($\theta_b = 22.1°$) than the lowest energy conformations of methyl, ethyl, isopropyl, or propyl (θ_b = 0–16°). The special role of hyperconjugation involving the α-CH bond which is eclipsed with the radical half-occupied orbital is indicated by the stretching of these bonds in *tert*-butyl (Table I) and in simpler radicals;[8] in fact, both types of CH bonds of **1** are 4–8 mÅ longer than those of **2**.[14]

The pyramidalization of the *tert*-butyl radical is one, especially large, manifestation of the influence of asymmetric perturbations on normally planar systems. We have recently shown that even alkenes and carbonyls, which have much higher out-of-plane bending force constants than radicals, also pyramidalize under the influence of a methyl group in an asymmetric conformation.[15] As predicted for alkenes and carbonyls,[15] the pyramidalization of radicals is expected to be especially large in rigid polycyclic systems, where bonds adjacent to radical centers are constrained to partially staggered geometries with respect to the radical center. In such systems, one face of the radical will be more accessible

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(10) Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University, Pittsburgh 1980.

(11) Carlsen, N. R.; Radom, L.; Riggs, N. V.; Rodwell, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2233 and references therein.

(12) We believe that this is the cause of the calculated result reported in ref. 5 that the *tert*-butyl radical is planar.

(13) Photoelectron spectra of the *tert*-butyl radical suggest an even higher barrier to inversion than is found in our calculations: Koenig, T.; Balle, T.; Snell, W. *J. Am. Chem. Soc.* **1975**, *97*, 662. Koenig, T.; Balle, T.; Chang, J. C. *Specrosc. Lett.* 1976, *9*, 755. Dyke, J.; Jonathan, N.; Lee, E.; Morris, A.; Winter, M. *Phys. Scr.* **1977**, *16*, 197. Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

(14) There is still an inevitable "chicken-and-egg-indeterminancy" in these arguments, since the reduction of torsional interaction in these systems is inextricably related to an alteration of hyperconjugative interactions, so a more precise definition of *the* orbital interaction responsible for pyramidalization has not been attempted. Precisely the same direction of pyramidalization is found for ethyl cation and anion, although to much different extents.[10]

(15) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

to attack by neutral or other radical species, and so significant reaction stereoselectivity should be observed.[16] The 2-norbornyl radical is perhaps the clearest example of this type.

Conclusion

The degree of pyramidalization of the *tert*-butyl radical is ~40% that of a perfect tetrahedron, and *tert*-butyl has a barrier to inversion on the order of 1 kcal/mol. The minimum energy inversion pathway involves simultaneous flattening of the radical center and rotation of the three methyl groups. The pyramidalization of *tert*-butyl arises from a simultaneous (and inseparable) minimization of torsional repulsions and maximization of anti-periplanar hyperconjugative stabilization. In effect, the radical, like alkanes, has a tendency to adopt a staggered conformation. This effect joins electronegative substituent effects (e.g., CF_3)[17] and angle strain effects[18] as an identified cause of pyramidalization of "normally" planar radicals.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work, and to Professor Jack Timberlake of the University of New Orleans for arousing our interest in radical calculations.

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Carbene Singlet–Triplet Gaps. Linear Correlations with Substituent π Donation

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Abstract: The singlet–triplet gaps from STO-3G calculations for methylene and 29 substituted methylenes correlate with theoretical and empirical measures of π donation by substituents. The π donors stabilize the singlet more than the triplet, while π acceptors have the opposite effect. Rough estimates of carbene singlet–triplet gaps can be made by using either calculated π charges in the corresponding substituted benzene or empirical $\sigma_R{}^\circ$ constants.

Although the parent carbene, methylene, is a ground-state triplet, substituted methylenes often have singlet ground states. π donation to the vacant p orbital of the singlet state is generally believed to be the most effective mechanism for singlet stabilization,[1,2] and strong computational support for this π donor mechanism of singlet stabilization has been reported by Feller, Borden, and Davidson.[3] However, Bauschlicher, Schaefer, and Bagus noted that the stability of the singlet state of a halocarbene relative to the triplet increases as the halogen electronegativity increases,[4,5] and Harrison, Liedtke, and Liebman proposed more generally that electronegative substituents differentially stabilize singlet carbenes, while electropositive substituents stabilize triplet carbenes.[6,7] The relevance of electronegativity and π effects to the geometries of substituted singlet carbenes has also been argued,[8,9] and π effects have been shown to determine the electrophilic or nucleophilic character of substituted carbenes.[10]

We wish to show that for substituted carbenes, there is a remarkably simple relationship between the singlet–triplet (ST) gap and the substituent π donor or π acceptor propensity, assessed both theoretically and empirically. Thus, while the electronegativity arguments described above are relevant to ST gaps caused by central atom changes,[7] they are unnecessary in understanding substituent effects on ST gaps.

Models for Singlet or Triplet Carbene Stabilization

The valence orbitals of singlet and triplet states of carbenes are represented schematically in Figure 1. Both species are bent (~102° and 136°, respectively) and have a relatively low-lying σ lone-pair orbital and higher-lying π (p in methylene) orbital. The dominant configuration of a singlet methylene is σ^2p^0, while that of a triplet is σ^1p^1. A relatively high-lying π orbital of a substituent will mix with the carbene π (p) orbital. This will stabilize the singlet more than the triplet, since two π electrons from the donor are stabilized through this mixing. The triplet will be stabilized less because the stabilization of the two π electrons of the donor will be partially counteracted by destabilization of one π electron of the carbene.

The influence of π acceptors depends on the geometry of the carbene. If the carbene geometry is like that shown for the donor substituent in Figure 1a, then the acceptor can only stabilize the triplet, while rotation of the acceptor group so that the π orbital is in-plane permits greater stabilization of the singlet than the triplet. This arises due to the two-electron interaction involving the singlet σ orbital and the acceptor in-plane π^* orbital for the

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[†] Louisiana State University and University of Pittsburgh.

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(3) (a) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* **1979**, *71*, 4987. (b) *Chem. Phys. Lett.* **1980**, *71*, 22.

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(5) Bauschlicher, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 5492.

(6) Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162.

(7) These arguments[6] were also applied to species which are isovalent with carbenes: SiH_2, $^+NH_2$, and $^+PH_2$. Here, electropositive central atoms favor the singlet state and electronegative the triplet state; π-donor effects are obviously absent in this series.

(8) Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1980**, 124.

(9) Pauling, L. *J. Chem. Soc., Chem. Commun.* **1980**, 688.

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