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Correlation of Singlet-Triplet Gaps for Aryl Carbenes Calculated by MINDO/3, MNDO, AM1, and PM3 with Hammett-Type Substituent Constants

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Heats of formation, atomic charges, and geometries of some 110 structures involving substituted singlet and triplet phenyl and 4,4-dimethyl-1,4-dihydronaphthalene carbenes and the corresponding diazomethanes were calculated by MINDO/3, MNDO, AM1, and PM3 semiempirical molecular orbital methods. The singlet-triplet gaps for AM1 and PM3 calculations for the *para* derivatives in both systems have been successfully correlated with Brown σ^+ constants. Good correlations with σ^+ were found for the charges on the carbenic centers of the singlets as well as with the energy barrier for rotation of the aryl group about the C-C single bond in substituted singlet phenylcarbenes. Comparisons of these results with experimental data indicate that AM1 and PM3 are much better than MNDO and MINDO/3 in predicting the intrinsic substituent effects in singlet carbenes.

INTRODUCTION

Carbene chemistry has become of considerable interest to both synthetic and mechanistic organic chemists since Hine demonstrated the intermediacy of dichlorocarbene in 1950.¹ Subsequently, the chemistry of these highly reactive intermediates in liquid solution² and in rigid media³ has been extensively investigated. Over the past two decades reports have also appeared in the literature concerning quantitative correlations between structure and reactivity of carbenes.^{2b,4-7} The vast majority of these studies are of olefinic selectivities of aliphatic carbenes,⁴ such as CF₂, CFCI, and CCl₂, and of substituent effects on the reactivity and selectivity of arylcarbenes.^{2,8} The recent studies in solution on the effect of ring substituents on the reactivity and selectivity of rigid and nonrigid arylcarbenes suggest that ring substituents could affect either the singlet-triplet intersystem crossing⁷ or the electrophilicity of the singlets.^{5,6} The findings that the stereospecificity and the regioselectivity in the addition of arylcarbenes to *cis*-2-butene and 1,1-dimethylallene, respectively, were increased as the substituents were changed from electron-withdrawing to electron-donating groups indicate that with singlet-stabilizing substituents (electron-donating groups), the degree of singlet involvement can be increased and with electron-withdrawing groups increasing amounts of triplet chemistry can be seen.⁷ In contrast, studies on the

effect of ring substituents on the relative rates of addition and O-H and C-H bond insertion by substituted phenylcarbenes and on the pyrolysis of rigid aryldiazomethanes in methanol support the argument that the major effect of ring substituents is on the electrophilicity of the singlets rather than on the intersystem crossing.^{5,6} On the other hand, recent laser spectrophotometric studies indicate that the singlet-triplet gap is a sensitive function of the carbene and that its magnitude largely determines the chemical properties of these species.⁹

Although the singlet-triplet gaps for some aliphatic and aromatic carbenes have been measured directly by spectroscopic methods such as high-speed pulsed spectroscopy,¹⁰⁻¹² these studies still remain insufficient. There is a need for a theory to provide information about geometries, charge distributions, singlet-triplet gaps, and electrophilic and nucleophilic characteristics of a wide variety of carbenes which could contribute to the understanding of their nature and chemical behavior.

Quantum mechanical calculations based on *ab initio* and semiempirical self-consistent field molecular orbital (SCF-MO) theories have become very important tools for the investigation of the structure and reactivity of neutral and ionic species as sophisticated computers have become more readily available.¹³

The history of the interplay between *ab initio* methods and experiment is rich in many examples that demonstrate a considerable contribution to the resolution of a variety of problems. However, such synergistic interactions are presently limited to rel-

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atively small systems due to resource limitations and to the long times required for calculations performed by *ab initio* SCF-MO procedures.¹⁴ There is therefore a pressing need for a general procedure for studying the properties of large molecules. Systematic studies of neutral molecules,¹⁵ carbenes,¹⁶ excited states,¹⁷ electron affinities and anions,¹⁸ proton affinities,¹⁹ cations,²⁰ and radical cations²¹ by semiempirical molecular orbital methods such as MINDO/3, MNDO, and AM1 demonstrate the powerful ability of these methods in predicting geometries and heats of formation of reactive species.

The application of semiempirical molecular orbital theory to the study of carbenes has been known for over two decades. Although these methods tend to underestimate the absolute singlet-triplet energy gaps for carbenes, they give good comparative results in a graduated series. The vast majority of these calculations have been directed toward the study of methylene (the simplest carbene).²² Recently, Schuster and Li applied these semiempirical methods to a systematic study of a wide variety of arylcarbenes.¹⁶ Their work shows that MINDO/3, MNDO, and AM1 calculations give values of singlet-triplet gaps that are approximately linearly related to the experimental estimates of the energy gap. On the other hand, to our knowledge, there are no reports in the literature on the relationships between substituent constants (Hammett type) and calculated properties of arylcarbenes by MINDO/3, MNDO, AM1, and PM3 semiempirical molecular orbital methods. We report here a study of the relationships between substituent effects and semiempirically calculated properties of substituted phenylcarbenes and substituted 4,4-dimethyl-1,4-dihydronaphthalene carbenes. Our choice is justified by the fact that experimental data for these systems are available and hence direct comparisons may be made with results of our study.

METHODS

All computations were done on a Cray X-MP/28 computer with use of MOPAC version 5.0 (QCPE No. 455).^{23a} The starting geometries were obtained from the PCMODEL program.^{23b} The calculations were carried out by the standard MNDO,²⁴ AM1,²⁵ MINDO/3,^{15a} and PM3²⁶ programs. Geometries were optimized in internal coordinates and the calculations were terminated when the change in energy on successive iterations was less than 0.00001 kcal/mol and the change in density matrix elements on two successive iterations was less than 0.001. The energies for the triplet carbenes and the corresponding diazomethanes were calculated by both the restricted and the unrestricted Hartree-Fock methods (RHF and UHF, respectively). The singlet states were calculated by the RHF method, but without configuration interaction (CI). The activation energy of a

certain pathway was checked by the "reaction coordinate" method.²⁷ All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles) without imposition of symmetry restrictions. Since an energy of an organic molecule is strongly dependent on its conformation, we were concerned with the identification of the most stable conformation of each of the substituted phenylcarbenes. This was accomplished by rotation of the substituent about the bond leading to the phenyl ring and calculation of the attendant conformational energies. In the calculations for the *meta*- and *para*-hydroxyphenylcarbenes, the starting geometries were begun where the hydroxy proton is coplanar to the phenyl ring. In all the cases, it was found that the conformation with a planar hydroxy group is the more stable one. In the calculations of *para*-amino arylcarbenes, two particular types of conformations were examined: one where the amine moiety is pyramidal and the other where it is planar. In all cases, it was found that the global minimum conformation is with pyramidal amino group. In the cases of *meta*- and *para*-methoxyarylcarbenes, two types of conformations were also considered: the one where the methoxy group is coplanar to the phenyl ring and the other where it is perpendicular. In the calculations of *para*-carbomethoxyarylcarbenes the two conformations considered in particular were the one where the carbonyl group is perpendicular to the phenyl ring and the other where it is coplanar. For all the conformations considered, the one with the lowest energy was selected for the correlation analysis.

RESULTS AND DISCUSSION

The present computational study is based upon 110 structures involving substituted phenyl (PC) and 4,4-dimethyl-1,4-dihydronaphthalene carbenes (DDNC) and the corresponding diazomethanes. The selection of the derivatives was made on the basis of the diverse physicochemical properties of the substituent groups.

The computed properties of *para*- and *meta*-substituted phenylcarbenes are shown in Tables I-V, whereas Tables VI and VII summarize the properties of *para*-substituted DDNC carbenes. The values given in Table I include the calculated heats of formation of *para*-substituted singlet, $(\Delta H_f^0)_S$ and triplet, $(\Delta H_f^0)_{T1}$ and $(\Delta H_f^0)_{T2}$ phenylcarbenes. The value $(\Delta H_f^0)_{T1}$ corresponds to the calculated properties of triplets by the UHF method and $(\Delta H_f^0)_{T2}$ corresponds to those computed by the RHF method. Also included are the calculated singlet-triplet energy gaps, $(\Delta H_f^0)_{T1S}$ and $(\Delta H_f^0)_{T2S}$ for the *para*-substituted derivatives. Table II lists the heats of formation of substituted phenyldiazomethanes $(\Delta H_f^0)_{XC_6H_4CHN_2}$ and the calculated energy differences for the isodesmic pro-

Table I. Calculated heats of formation and single-triplet gaps (kcal/mol) for *para*-substituted phenylcarbenes.

<i>X</i>	MINDO/3					MNDO				
	(ΔH_f^0) _s	(ΔH_f^0) _{T1}	(ΔH_f^0) _{T2}	(ΔH_f^0) _{T1S} ^b	(ΔH_f^0) _{T2S} ^c	(ΔH_f^0) _s	(ΔH_f^0) _{T1}	(ΔH_f^0) _{T2}	(ΔH_f^0) _{T1S} ^b	(ΔH_f^0) _{T2S} ^c
<i>p</i> -NH ₂	98.0	79.77	100.11	-18.23	2.12	116.34	74.30	98.53	-42.04	-17.81
<i>p</i> -OH	52.28	33.62	53.69	-18.66	1.41	67.93	25.83	49.95	-42.10	-17.98
<i>p</i> -OMe	62.23	44.32	63.77	-17.91	1.54	77.72	34.62	58.67	-43.10	-19.05
<i>p</i> -Me	107.42	84.52	105.21	-22.90	-2.21	109.72	66.65	90.47	-43.07	-19.25
<i>p</i> -Et	101.70	78.92	99.52	-22.78	-2.18	104.94	61.88	85.68	-43.06	-19.26
<i>p</i> - <i>i</i> -Pr	104.87	81.94	102.63	-22.93	-2.24	109.61	61.33	90.10	-48.28	-19.51
<i>p</i> - <i>t</i> -Bu	120.49	97.46	118.33	-23.03	-2.16	111.74	68.70	92.72	-43.04	-19.02
H	113.75	91.53	111.55	-22.22	-2.20	118.24	74.81	98.28	-43.43	-19.96
<i>p</i> -Cl	104.99	83.43	103.81	-21.53	-1.18	110.38	66.74	90.23	-43.64	-20.15
<i>p</i> -Br	—	—	—	—	—	120.69	77.13	100.71	-43.56	-19.98
<i>p</i> -COOMe	21.39	-2.44	17.95	-23.83	-3.44	36.57	-6.68	16.54	-43.25	-20.03
<i>p</i> -CF ₃	-60.55	-58.36	-63.87	2.19 ^a	-3.32	-31.29	-73.84	-50.99	-42.55	-19.70
<i>p</i> -CN	135.65	111.25	132.26	-24.4	-3.39	148.53	105.23	128.85	-43.30	-19.68
<i>p</i> -NO ₂	95.14	71.11	91.28	-24.03	-3.86	132.47	88.82	112.28	-43.65	-20.19

	AM1					PM3					σ^+ ^d
	(ΔH_f^0) _s	(ΔH_f^0) _{T1}	(ΔH_f^0) _{T2}	(ΔH_f^0) _{T1S} ^b	(ΔH_f^0) _{T2S} ^c	(ΔH_f^0) _s	(ΔH_f^0) _{T1}	(ΔH_f^0) _{T2}	(ΔH_f^0) _{T1S} ^b	(ΔH_f^0) _{T2S} ^c	
112.72	80.59	101.01	-32.13	-11.71	115.85	77.66	98.46	-38.19	-17.39	-1.3	
71.65	38.40	58.47	-33.25	-13.18	73.31	35.02	55.22	-38.29	-18.09	-0.92	
77.76	44.84	64.94	-32.92	-12.82	80.28	43.21	62.48	-37.07	-17.80	-0.78	
109.53	75.33	95.35	-34.20	-14.18	110.42	71.00	91.05	-39.42	-19.37	-0.311	
104.17	69.98	91.37	-34.19	-12.80	106.18	66.79	86.79	-39.39	-19.39	-0.3	
101.38	67.21	87.33	-34.17	-14.05	101.90	62.54	82.55	-39.36	-19.35	-0.28	
99.13	65.03	85.60	-34.10	-13.53	96.69	57.32	77.19	-39.37	-19.50	-0.26	
117.65	83.39	102.96	-34.26	-14.69	120.35	80.73	100.19	-39.62	-20.16	0	
110.87	75.69	95.79	-35.18	-15.08	113.80	73.55	93.77	-40.25	-20.03	0.114	
123.47	87.77	107.89	-35.70	-15.58	128.72	88.34	107.98	-40.38	-20.74	0.15	
36.71	0.41	20.35	-36.30	-16.36	40.51	-0.69	19.09	-41.20	-21.42	0.49	
-36.18	-72.59	-53.22	-36.41	-17.04	-35.63	-77.42	-58.09	-41.79	-22.46	0.62	
152.01	114.59	134.69	-37.42	-17.32	157.07	116.56	135.82	-40.51	-21.25	0.659	
124.15	87.16	106.79	-36.99	-17.36	113.99	72.51	91.58	-41.48	-22.41	0.79	

^aExcluded from the correlation analysis (see Table VIII).^bCalculated from (ΔH_f^0)_{T1S} = (ΔH_f^0)_{T1} - (ΔH_f^0)_s.^cCalculated from (ΔH_f^0)_{T2S} = (ΔH_f^0)_{T2} - ($\Delta H_f^0)_s.$ ^dTaken from reference 29.

cesses 1S and 1T, (ΔH_f^0)_{1S} and (ΔH_f^0)_{1T}, respectively (Scheme I). The calculated bond angles H1C2C3 (Θ) and dihedral angles H1C2C3C4 (λ) (Scheme I) of *para*-substituted singlet and triplet phenylcarbenes are depicted in Table III. Also included are the calculated energy barriers for the rotation of the aryl group about the C2C3 bond (E_{act}) (Scheme I.) Table IV lists the calculated atomic charges on the carbenic centers of *para*-substituted singlet and triplet phenylcarbenes, qC_S : and qC_{T1} :, respectively.

The heats of formation of *meta*-substituted singlet, (ΔH_f^0)_s, and triplet, (ΔH_f^0)_{T1}, phenylcarbenes and the atomic charges on the carbenic centers of the singlets, qC_S :, and the triplets, qC_{T1} :, are summarized in Table V. Table VI lists the AM1- and PM3-calculated singlet-triplet gaps [(ΔH_f^0)_{T1S} and ($\Delta H_f^0)_{T2S}] and the heats of formation of singlet [(ΔH_f^0)_s] and triplet [($\Delta H_f^0)_{T2} and ($\Delta H_f^0)_{T1}] 4,4-dimethyl-1,4-dihydronaphthalene carbenes. The properties shown in Table VII include AM1- and PM3-calculated bond angles C1C2C3 (Θ) and the atomic charges on the carbenic centers of singlet and triplet DDNC carbenes, qC_S : and qC_{T1} :, respectively. Also included are the cal-$$$

culated heats of formation of the corresponding diazomethanes ($\Delta H_{\text{XC12H12N2}}^0$) as well as the energy differences for the isodesmic processes 2S and 2T, (ΔH_r^0)_{S2} and (ΔH_r^0)_{T2}, respectively (Scheme II).

The results given in Tables I–VII were examined for linear relationships with σ ,²⁸ σ^+ ,²⁹ and σ^- .³⁰ The correlation results were found to follow reasonably well the expression shown in eq. (1), where *Y* is the variable parameter (see column 4 in Table VIII), *X* is σ , σ^+ , or σ^- , ρ_{calc} is the slope and *C* is the intercept.

The regression outputs of the semiempirical calculated singlet-triplet energy gaps for the PC and DDNC systems are shown as entries 1–6 and 22–25, respectively, in Table VIII. Entries 7–9 and 26–27 list those of the calculated energy differences for the isodesmic processes 1S and 2S, respectively. The values of the atomic charges on the carbenic centers of the singlet and triplet carbenes in both systems are shown as entries 10–21 and 28–31, respectively, in Table VIII. The regression outputs of the energy barrier (E_{act}) for the rotation of the aryl ring about C2C3 bond from a planar conformation (λ = 0°) to

$$Y = \rho_{\text{calc}} X + C \quad (1)$$

Table II. Calculated energies (kcal/mol) for processes 1S and 1T.^a

Substituent <i>X</i>	MINDO/3			MNDO		
	$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2$	$(\Delta H_f^\circ)_{1S}^d$	$(\Delta H_f^\circ)_{1T}$	$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2$	$(\Delta H_f^\circ)_{1S}^d$	$(\Delta H_f^\circ)_{1T}$
<i>p</i> -NH ₂	29.94	6.10	1.79	87.55	2.30	0.15
<i>p</i> -OH	-17.39	4.49	0.88	39.32	2.48	0.50
<i>p</i> -OMe	-7.49	4.44	0.70	48.29	1.66	0.75
<i>p</i> -Me	32.89	-0.37	-0.36	79.25	0.62	-0.09
<i>p</i> -Et	28.37	0.83	0.81	76.58	2.73	2.03
<i>p</i> - <i>i</i> -Pr	30.25	-0.46	-0.42	73.88	-4.64	-5.09
<i>p</i> - <i>t</i> -Bu	45.59	-0.74	-0.78	81.11	0.46	-0.48
H	39.59	0	0	87.15	0	0
<i>p</i> -Cl	31.69	0.86	-0.16	79.27	-0.02	0.17
<i>p</i> -Br	—	—	—	89.63	0.03	0.05
<i>p</i> -COOMe	-55.18	-2.41	-1.17	5.58	0.10	0.17
<i>p</i> -CF ₃	-137.53	-2.82	-1.70	-62.31	0.07	-0.19
<i>p</i> -CN	59.42	-2.07	-0.88	117.53	0.09	-0.19
<i>p</i> -NO ₂	66.34	45.36 ^c	-24.94	61.81	-39.57	-50.47

AM1				PM3			
$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2$	$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2^b$	$(\Delta H_f^\circ)_{1S}^d$	$(\Delta H_f^\circ)_{1T}^e$	$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2$	$\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2^b$	$(\Delta H_f^\circ)_{1S}^d$	$(\Delta H_f^\circ)_{1T}^e$
83.64	79.32	3.56	0.58	81.70	81.23	2.59	0.79
41.06	37.0	2.05	0.45	38.96	38.58	2.39	0.78
47.35	43.47	2.23	0.48	45.95	45.59	2.41	-0.4
77.33	73.60	0.44	0.12	74.28	74.05	0.60	0.27
72.01	68.28	0.48	0.15	70.73	70.46	1.29	0.89
68.03	64.37	-0.71	-0.99	65.08	64.98	-0.08	-0.34
66.52	62.88	0.03	-0.3	60.49	60.24	0.54	0.14
85.01	81.54	0	0	83.61	83.51	0	0
77.76	74.18	-0.47	0.34	76.94	76.62	-0.12	0.29
89.62	86.18	-1.21	0.26	91.22	91.09	-0.76	-0.03
1.30	-1.57	-2.77	-0.13	1.75	1.68	-2.02	-0.41
-71.67	-74.49	-2.85	-0.05	-75.22	-75.25	-2.85	-0.61
116.04	112.86	-2.16	0.12	118.38	118.24	-1.95	-1.10
70.22	66.81	-20.76 ^c	-1.85	73.73	73.71	-3.52 ^c	-1.58

^aThe energies were calculated by RHF method except as indicated.^bThe energies were calculated by UHF method.^cExcluded from the correlation analysis, see Table VIII.^dCalculated from $(\Delta H_f^\circ)_{1S} = (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CH})_S - (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CHN}_2) - (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CH})_S + (\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2)$.^eCalculated from $(\Delta H_f^\circ)_{1T} = (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CH})_{T1} - (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CHN}_2)^b - (\Delta H_f^\circ \text{C}_6\text{H}_4\text{CH})_{T1} + (\Delta H_f^\circ \text{XC}_6\text{H}_4\text{CHN}_2)^b$.

a perpendicular conformation ($\lambda = 90^\circ$) in substituted singlet phenylcarbenes are listed as entries 16 and 17 in Table VIII.

Examination of the results (Table VIII) reveals that, on the whole, there is a satisfactory correlation between the experimentally derived *X* (σ , σ^+ , and σ^-) and the calculated properties *Y* (see Table VIII). However, the correlation of the calculated MINDO/3 properties were found to be significantly inferior to those of both the AM1 and PM3 methods. Attempted regressions of σ , σ^+ , or σ^- with either the MNDO-calculated properties of the phenylcarbene system or the MNDO-calculated energy differences for the isodesmic processes $1T[\Delta H_f^\circ]_{1T}$ and $2T[(\Delta H_f^\circ)_{2T}]$ failed (r^2 less than 40%). Although a good correlation was found for AM1- and PM3-calculated atomic charges on the carbenic centers of *meta*-substituted singlet and triplet phenylcarbenes, the regression outputs of the singlet-triplet gaps gave r^2 values equaling less than 45%.

Examination of Tables II and VII indicates a few

systematic deviations which become pronounced and whose significance may be understood. For example, the usually stated explanation of the effect of substituents on the stability (selectivity) of substituted phenyl⁵ and 4,4-dimethyl-1,4-dihydronaphthalene⁶ carbenes is fundamentally valid. Electron-donating groups (e.g., NH₂, OH) are singlet stabilizing substituents, whereas electron-withdrawing groups (e.g., CF₃, CN) are singlet destabilizing substituents. For example, the AM1-calculated $(\Delta H_f^\circ)_{1S}$ value of *p*-NH₂ is 3.56, whereas that of *p*-CN is -2.16 (entries 1 vs. 13 in Table II). This observation is not surprising since singlet phenyl and 4,4-dimethyl-1,4-dihydronaphthalene carbene systems are seen to be isoelectronic with a benzylic cation system. This conclusion is also supported by the calculated atomic charges, q_{C_S} , listed in Tables IV, V, and VII, which show that the charges on the carbenic centers of substituted singlet PC and DDNC carbenes were increased as the substituents were changed from electron-donating to electron-withdrawing groups.

Table III. Calculated properties for singlet and triplet phenylcarbenes.^{a,b}

MINDO/3					MNDO			
Substituent	Singlet		Triplet		Singlet		Triplet	
<i>X</i>	Θ	λ	Θ	λ	Θ	λ	Θ	λ
<i>p</i> -NH ₂	109.9	-0.4	143.1	0.6	120.3	2.9	164.0	-0.3
<i>p</i> -OH	109.7	0	143.1	0	120.0	0.2	164.9	0
<i>p</i> -OMe	109.7	0.8	142.7	-0.3	120.0	4.1	164.8	0.5
<i>p</i> -Me	109.4	-0.2	143.0	-0.1	120.4	-18.5	163.8	-0.3
<i>p</i> -Et	109.6	-179.8	143.1	-0.1	119.5	-0.6	164.5	0.6
<i>p</i> - <i>i</i> -Pr	109.5	-3.1	143.2	179.9	122.4	122.1	164.8	2.7
<i>p</i> - <i>t</i> -Bu	109.6	0.6	143.0	179.8	119.8	-8.4	164.1	179.8
H	109.6	-4.2	143.0	-179.8	122.6	-92.4	163.9	-179.1
<i>p</i> -Cl	109.5	179.2	143.0	180.0	124.0	-91.1	179.6	38.7
<i>p</i> -Br	—	—	—	—	124.2	-98.3	164.3	-178.6
<i>p</i> -COOMe	104.5	-97.7	142.9	0.2	125.2	-85.3	171.5	0.2
<i>p</i> -CF ₃	111.2	-93.6	144.6	-0.6	127.8	-93.0	165.6	-0.5
<i>p</i> -CN	110.4	-92.9	143.1	-179.3	126.0	-93.6	164.2	-179.4
<i>p</i> -NO ₂	110.2	-105.1	143.3	0.2	127.9	-92.7	165.5	-179.8

AM1					PM3				
Singlet			Triplet		Singlet			Triplet	
Θ	λ	<i>E</i> _{act}	Θ	λ	Θ	λ	<i>E</i> _{act}	Θ	λ
116.3	180.0	6.80	154.4	-0.4	112.1	0.0	5.52	151.6	-0.6
116.0	-0.1	5.37	155.4	0.1	112.1	-0.4	5.39	151.5	0.0
116.1	-0.6	5.64	154.9	-0.1	112.3	0.6	5.47	151.2	0.2
115.9	-1.1	3.63	155.2	0.1	111.9	-0.1	3.66	151.5	-0.5
115.8	-1.0	—	154.8	0.2	111.9	-0.5	—	151.4	0.5
115.9	-179.9	—	154.9	-179.5	111.9	-179.9	—	151.4	-179.3
115.5	-179.0	—	154.8	-179.8	111.9	-179.0	—	151.3	-179.9
115.8	-197.5	3.15	154.8	-179.9	111.9	-178.7	3.10	150.8	-179.9
115.9	-0.2	2.85	155.1	179.9	111.9	-178.8	2.97	151.5	-179.9
115.8	-3.5	—	155.1	179.9	111.9	-179.1	—	151.5	-179.7
115.7	0.7	1.32	155.2	0	111.7	3.2	1.50	151.6	0
116.8	-27.4	0.50	155.2	0.1	112.2	-28.6	0.51	151.8	-0.5
119.6	-10.2	1.16	156.2	-180.0	112.0	-12.2	1.36	151.6	65.3
117.3	-88.9	-0.83 ^c	154.0	0.3	114.3	-86.9	-1.41 ^c	152.1	-0.1

^aThe singlet and triplet properties were calculated by RHF and UHF methods, respectively.^bThe bond (Θ) and the dihedral (λ) angles are in deg units. The activation barrier (E_{act}) is in kcal/mol.^cThe negative sign indicates that the perpendicular conformation is more stable than the planar conformation (see text).**Table IV.** Calculated atomic charges for singlet and triplet phenylcarbenes.^a

Substituent <i>X</i>	MINDO3		MNDO		AM1		PM3	
	$qC:s$	$qC:\pi$	$qC:s$	$qC:\pi$	$qC:s$	$qC:\pi$	$qC:s$	$qC:\pi$
<i>p</i> -NH ₂	-0.0588	-0.1423	-0.0403	-0.1900	-0.0945	-0.2778	0.0024	-0.2130
<i>p</i> -OH	-0.0338	-0.1350	-0.0373	-0.1908	-0.0713	-0.2479	0.0135	-0.2035
<i>p</i> -OMe	-0.0368	-0.1305	-0.0277	-0.1871	-0.0750	-0.2469	0.0086	-0.1955
<i>p</i> -Me	-0.0092	-0.1295	-0.0187	-0.1873	-0.0627	-0.2364	0.0269	-0.1857
<i>p</i> -Et	-0.0094	-0.1301	-0.0224	-0.1879	-0.0625	-0.2782	0.0268	-0.1824
<i>p</i> - <i>i</i> -Pr	-0.0075	-0.1297	0.0445	-0.1894	-0.0630	-0.2438	0.0265	-0.1827
<i>p</i> - <i>t</i> -Bu	-0.0079	-0.1286	-0.0214	-0.1872	-0.0594	-0.2781	0.0279	-0.1848
H	-0.0074	-0.1309	0.0751	-0.1890	-0.0572	-0.2316	0.0343	-0.1748
<i>p</i> -Cl	0.0045	-0.1242	0.0765	-0.2001	-0.0536	-0.2214	0.0363	-0.1692
<i>p</i> -Br	—	—	0.0734	-0.1816	-0.0478	-0.2192	0.0426	-0.1608
<i>p</i> -COOMe	0.0765	-0.1182	0.0697	-0.1936	-0.0409	-0.2133	0.0537	-0.1404
<i>p</i> -CF ₃	0.0819	-0.1205	0.0676	-0.1737	-0.0237	-0.1940	0.0849	-0.1304
<i>p</i> -CN	0.0774	-0.1242	0.0704	-0.1767	0.0530 ^b	-0.2011 ^b	0.0573	-0.1415 ^b
<i>p</i> -NO ₂	0.0781	-0.1109	0.0724	-0.1699	-0.0080	-0.1973	0.1942 ^b	-0.1042

^aAtomic charges for singlets and triplets were calculated by RHF and UHF methods, respectively.^bExcluded from the correlation analysis (see Table VIII).

Table V. Calculated properties for meta-substituted phenylcarbenes by AM1 and PM3 methods.^a

Substituent <i>X</i>	AM1						<i>qC</i> : _s	<i>qC</i> : _T ^b
	(ΔH_f°) _s	(ΔH_f°) _{T1} ^b	(ΔH_f°) _{T2}	(ΔH_f°) _{T1S} ^d	(ΔH_f°) _{T2S} ^e			
<i>m</i> -Me	110.09	75.69	95.55	-34.40	-14.54	-0.0565	-0.2356	
<i>m</i> -Et	104.42	70.03	89.71	-34.39	-14.71	-0.0577	-0.2331	
<i>m-i</i> -Pr	101.62	66.31	86.37	-34.17	-15.25	-0.0577	-0.2361	
<i>m-t</i> -Bu	99.36	64.97	84.88	-34.39	-14.48	-0.0593	-0.2382	
H	117.65	83.39	102.96	-34.26	-14.69	-0.0572	-0.2357	
<i>m</i> -OH	74.88	39.28	59.06	-35.60	-15.82	-0.0434 ^c	-0.2290	
<i>m</i> -OMe	80.57	45.40	65.38	-35.17	-15.19	-0.0509	-0.2331	
<i>m</i> -COOMe	35.26	0.87	20.31	-34.39	-14.95	-0.0464	-0.2275	
<i>m</i> -Cl	111.15	76.14	96.18	-35.01	-14.97	-0.0483	-0.2270	
<i>m</i> -Br	122.93	88.22	108.20	-34.71	-14.73	-0.0496	-0.2282	
<i>m</i> -CF ₃	-37.73	-72.30	-52.93	-34.57	-15.20	-0.0445	-0.2208	
<i>m</i> -CN	150.04	115.08	134.80	-34.96	-15.24	-0.0454	-0.2244	
<i>m</i> -NO ₂	122.80	87.68	107.11	-35.12	-15.69	-0.0343	-0.2162	

PM3							<i>qC</i> : _s	<i>qC</i> : _T ^b
(ΔH_f°) _s	(ΔH_f°) _{T1} ^b	(ΔH_f°) _{T2}	(ΔH_f°) _{T1S} ^d	(ΔH_f°) _{T2S} ^e				
111.04	71.29	90.93	-39.75	-20.11	0.0346	-0.1906		
106.65	66.66	88.14	-39.99	-18.51	0.0335	-0.1944		
102.47	62.84	82.53	-39.63	-19.94	0.0332	-0.1914		
97.15	57.56	77.19	-39.59	-19.96	0.0329	-0.1937		
120.35	80.73	100.19	-39.62	-20.16	0.0343	-0.1883		
76.52	35.65	55.27	-40.87	-21.25	0.0473 ^c	-0.1868		
83.74	43.51	62.37	-40.23	-21.37	0.0379	-0.1852		
39.61	-0.40	19.00	-40.01	-20.61	0.0490	-0.1798		
114.34	73.87	93.65	-40.47	-20.69	0.0442	-0.1842		
128.57	88.34	108.00	-40.23	-20.57	0.0530	-0.1810		
-36.90	-77.25	-57.88	-40.35	-20.98	0.0530	-0.1764		
156.59	115.91	135.54	-40.68	-21.05	0.0537	-0.1788		
113.07	72.73	91.84	-40.34	-21.23	0.0639	-0.1701		

^aThe energies (kcal/mol) were calculated by RHF methods except as indicated.^bCalculated by UHF method.^cExcluded from the correlation analysis (see Table VIII).^dSee Table I, note b.^eSee Table I, note c.**Table VI.** Calculated heats of formation and singlet-triplet gap (kcal/mol) for para-substituted 4,4-dimethyl-1,4-dihydronaphthalene carbenes.^a

Substituent <i>X</i>	AM1					PM3				
	(ΔH_f°) _s	(ΔH_f°) _{T1} ^b	(ΔH_f°) _{T2}	(ΔH_f°) _{T1S} ^c	(ΔH_f°) _{T2S} ^d	(ΔH_f°) _s	(ΔH_f°) _{T1} ^b	(ΔH_f°) _{T2}	(ΔH_f°) _{T1S} ^c	(ΔH_f°) _{T2S} ^d
<i>p</i> -OH	67.09	39.36	60.48	-27.73	-6.61	62.89	32.61	52.55	-30.28	-10.34
<i>p</i> -OMe	73.94	46.0	67.03	-27.94	-6.91	70.56	40.03	59.84	-30.53	-10.72
<i>p</i> -Me	104.94	76.22	97.13	-28.72	-7.81	100.17	68.56	88.29	-31.61	-11.88
<i>p-t</i> -Bu	94.24	65.62	86.89	-28.62	-7.35	86.20	54.86	74.48	-31.34	-11.72
<i>p</i> -F	67.18	38.17	59.68	-29.01	-7.50	65.78	34.21	54.03	-31.57	-11.75
H	113.35	84.65	104.97	-28.70	-8.38	110.12	78.39	97.72	-31.73	-12.40
<i>p</i> -Cl	105.73	76.61	97.73	-29.12	-8.0	102.83	71.07	91.0	-31.82	-11.83
<i>p</i> -Br	118.13	88.66	109.88	-29.47	-8.25	117.45	85.63	105.09	-31.82	-12.36
<i>p</i> -COOMe	31.44	1.19	22.01	-30.25	-9.43	29.15	-3.02	16.51	-32.17	-12.64
<i>p</i> -CF ₃	-42.15	-71.91	-51.41	-29.76	-9.26	-47.36	-80.0	-60.64	-32.64	-13.28
<i>p</i> -CN	145.22	115.44	136.63	-29.78	-8.59	145.59	113.05	133.09	-32.54	-12.50
<i>p</i> -NO ₂	118.0	87.71	108.52	-30.29	-9.48	102.94	69.62	88.97	-33.32	-13.97

^aThe energies were calculated by RHF method except as indicated.^bCalculated by UHF method.^cSee Table I, note b.^dSee Table I, note c.

Table VII. Computed properties for para-substituted 4,4-dimethyl-1,4-dihydronaphthalene carbenes ($C_{12}H_{12}$) and calculated energies (kcal/mol) for processes 2S and 2T.^a

Substituent <i>X</i>	AM1							
	$\Delta H_f^\circ XC_{12}H_{12}N_2$	$\Delta H_f^\circ XC_{10}H_{10}N_2^b$	$(\Delta H_r^\circ)_{2S}^d$	$(\Delta H_r^\circ)_{2T}^e$	Θ Singlet	Θ^b Triplet	$qC:s$	$qC:t$ ^b
<i>p</i> -OH	50.17	44.10	2.43	2.87	116.9	129.6	-0.0472	-0.0814
<i>p</i> -OMe	56.67	48.45	2.08	0.58	116.9	129.9	-0.0426	-0.0820
<i>p</i> -Me	86.48	78.62	0.89	0.53	116.8	129.8	-0.0385	-0.0830
<i>p</i> - <i>t</i> -Bu	75.72	67.87	0.83	0.38	116.6	129.6	-0.0394	-0.0827
<i>p</i> -F	48.95	42.96	1.12	2.92	116.6	129.8	-0.0345	-0.0785
H	94.0	86.52	0	0	115.4	130.0	-0.0186 ^c	-0.0840
<i>p</i> -Cl	86.82	81.18	0.44	2.70	116.7	129.7	-0.0339	-0.0788
<i>p</i> -Br	98.61	93.18	-0.17	2.65	116.5	129.7	-0.0284	-0.0782
<i>p</i> -COOMe	17.27	10.52	5.18 ^c	7.46	116.2	129.5	-0.0224	-0.0770
<i>p</i> -CF ₃	-62.65	-69.17	-1.15	0.87	116.5	129.7	-0.0226	-0.0758
<i>p</i> -CN	125.19	118.19	-0.68	0.88	116.9	129.7	-0.0309 ^c	-0.0766
<i>p</i> -NO ₂	96.65	90.65	-2.0	1.07	117.0	129.7	-0.0230	-0.0714

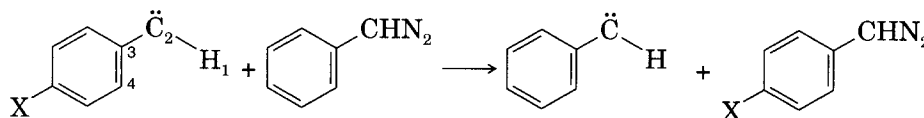
PM3							
$\Delta H_f^\circ XC_{12}H_{12}N_2$	$\Delta H_f^\circ XC_{12}H_{12}N_2^b$	$(\Delta H_r^\circ)_{2S}^d$	$(\Delta H_r^\circ)_{2T}^e$	Θ Singlet	Θ^b Triplet	$qC:s$	$qC:t$ ^b
41.21	40.12	2.51	1.22	115.6	130.2	-0.0224	-0.0790
48.24	46.47	1.87	0.15	115.6	130.0	-0.0166	-0.0777
76.69	75.79	0.71	0.94	115.0	130.1	0.0150 ^c	-0.0793
62.82	61.32	0.81	0.17	115.5	130.1	-0.0119	-0.0790
42.55	41.70	0.96	1.20	115.8	130.1	-0.0089	-0.0752
85.93	84.68	0	0	114.5	129.2	-0.0207 ^c	-0.0744
79.20	78.37	0.56	1.01	115.6	130.0	-0.0072	-0.0762
93.53	92.87	0.27	0.95	115.5	130.3	-0.0031	-0.0772
5.17	4.54	0.21 ^c	1.27	115.4	130.1	-0.0028	-0.0747
-73.01	-73.11	-1.46	0.60	115.6	129.7	0.0043	-0.0708
120.94	120.12	-0.46	0.78	115.4	130.0	0.0049	-0.0733
76.13	76.76	-2.62	0.85	115.5	129.8	0.0125	-0.0686

^aCalculated by RHF method except as indicated.^bCalculated by UHF method.^cExcluded from the correlation analysis, see Table VIII.^dCalculated from $(\Delta H_r^\circ)_{2S} = (\Delta H_f^\circ C_{12}H_{12})_S - (\Delta H_f^\circ C_{12}H_{12}N_2) - (\Delta H_f^\circ XC_{12}H_{12})_S + (\Delta H_f^\circ XC_{12}H_{12}N_2)$.^eCalculated from $(\Delta H_r^\circ)_{2T} = (\Delta H_f^\circ C_{12}H_{12})_T - (\Delta H_f^\circ C_{12}H_{12}N_2)^b - (\Delta H_f^\circ XC_{12}H_{12})_T + (\Delta H_f^\circ XC_{12}H_{12}N_2)^b$.

Conformational effects may be expected to influence the properties of substituted singlet phenylcarbenes, especially in light of evidence indicating that electron-donating substituents favor a planar conformation for a singlet carbene in order to stabilize the vacant *p* orbital, whereas electron-withdrawing groups are presumed to enhance twisting of the phenyl ring to a perpendicular conformation in which the electron-rich carbenic σ orbital is also favorably delocalized.^{8,31} This conclusion is mainly based on the fact that thermolyses of substituted diphenyldiazomethanes were facilitated either by electron-withdrawing or electron-donating groups.⁸ In order to examine this notion we investigated by AM1 and PM3 methods the relationship between sub-

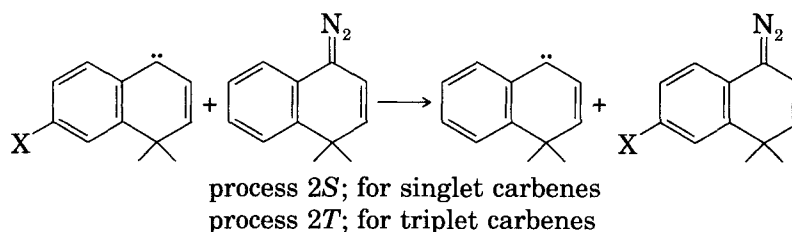
stituent effects and the energy barrier (E_{act}) for rotation of the aryl ring about the C2C3 bond in substituted singlet phenylcarbenes (for the numbering of the atoms see Scheme 1). The results of this study are summarized in Table III. A reasonably good correlation with σ^+ values was found (see entries 16 and 17 in Table VIII). Examination of these results indicates that the barrier to rotation (E_{act}) is strongly dependent upon the nature of the substituent. Thus rotations of the aryl group with strong electron-donating substituents have higher barriers than those with strong withdrawing groups ($E_{act} > 5$ kcal vs. $E_{act} < 1.5$ kcal; see Table III).

Another significant result observed is the effect of substituents on the optimum conformation of



process 1S; for singlet carbenes
process 1T; for triplet carbenes

Scheme 1.



Scheme 2.

the aryl ring. In all the substituents studied except $p\text{-NO}_2$, it was found that the global optimum geometry is with a planar conformation of the aryl ring ($\lambda_{\text{H1C2C3C4}} \approx 0^\circ$ or 180°), whereas for $p\text{-NO}_2$ a perpendicular conformation is favorably populated ($\lambda_{\text{H1C2C3C4}} \approx 90^\circ$; see Table III). Since the energy barrier for ring rotation in the cases of electron-withdrawing groups is less than 1.5 kcal, it is likely that a fair amount of conformational flexibility should be manifested in the structure of the molecule. On the other hand, the MINDO/3-calculated results of the aryl ring rotation indicate that electron-donating sub-

stituents favor a planar conformation, whereas electron-withdrawing groups tend to enhance twisting of the aryl ring to a perpendicular conformation (see Table II). Based on the previous MINDO/3 study results which indicated that with electron-withdrawing groups the barrier to rotation of the aryl group is very small (0.6 kcal),³¹ it may be concluded that these structures have a large amount of conformational flexibility, similar to that concluded from the AM1 and PM3 calculations.

The energy difference between the triplet and the singlet states of a carbene, $(\Delta H_f^0)_{TS}$, in large part con-

Table VIII. Correlation of calculated and experimental properties of substituted phenylcarbenes (PC) and substituted 4,4-dimethyl-1,4-dihydronaphthalenecarbenes (DDNC) from the equation $Y = \rho_{\text{calc}} X + C$.

Entry	System	Method	Y	X	ρ_{calc}	C	n	r
1	para PC	AM1	$(\Delta H_f^0)_{T1S}$	σ^+	-2.46 ± 0.17	-35.03 ± 0.39	14	0.975
2	para PC	PM3	$(\Delta H_f^0)_{T1S}$	σ^+	-1.94 ± 0.24	-39.92 ± 0.55	14	0.917
3	para PC	MINDO/3	$(\Delta H_f^0)_{T1S}$	σ^+	-3.14 ± 0.59	-22.42 ± 1.23	12	0.860
4	para PC	AM1	$(\Delta H_f^0)_{T2S}$	σ^+	-2.95 ± 0.29	-14.93 ± 0.55	14	0.959
5	para PC	PM3	$(\Delta H_f^0)_{T2S}$	σ^+	-2.48 ± 0.16	-20.19 ± 0.37	14	0.975
6	para PC	MINDO/3	$(\Delta H_f^0)_{T2S}$	σ^+	-2.85 ± 0.39	-1.95 ± 0.88	13	0.911
7	para PC	AM1	$(\Delta H_f^0)_{1S}$	σ^+	-3.16 ± 0.24	-0.62 ± 0.49	13	0.971
8	para PC	PM3	$(\Delta H_f^0)_{1S}$	σ^+	-2.83 ± 0.25	-0.31 ± 0.25	13	0.960
9	para PC	MINDO/3	$(\Delta H_f^0)_{1S}$	σ^+	-4.38 ± 0.57	-0.17 ± 1.15	12	0.927
10 ^a	para PC	AM1	$qC:s$	σ	5.30 ± 0.41	-5.64 ± 0.57	13	0.970
11 ^a	para PC	PM3	$qC:s$	σ^+	3.45 ± 0.42	3.96 ± 0.87	13	0.927
12 ^a	para PC	MINDO/3	$qC:s$	σ^+	7.24 ± 0.77	1.89 ± 1.72	13	0.943
13 ^a	para PC	AM1	$qC:\tau_1$	σ^-	2.08 ± 0.16	-23.41 ± 0.25	13	0.971
14 ^a	para PC	PM3	$qC:\tau_1$	σ^-	1.77 ± 0.14	-18.89 ± 0.22	13	0.970
15 ^a	para PC	MINDO/3	$qC:\tau_1$	σ	1.11 ± 0.15	-12.60 ± 0.34	13	0.911
16	para PC	AM1	E_{act}	σ^+	-3.28 ± 0.23	2.75 ± 0.51	10	0.980
17	para PC	PM3	E_{act}	σ^+	-2.98 ± 0.37	2.61 ± 0.82	10	0.943
18 ^a	meta PC	AM1	$qC:s$	σ	2.52 ± 0.24	-5.61 ± 0.23	12	0.957
19 ^a	meta PC	PM3	$qC:s$	σ^+	3.63 ± 0.28	3.53 ± 0.26	12	0.975
20 ^a	meta PC	AM1	$qC:\tau_1$	σ	2.27 ± 0.24	-23.43 ± 0.23	13	0.943
21 ^a	meta PC	PM3	$qC:\tau_1$	σ	2.55 ± 0.23	-18.99 ± 0.22	13	0.957
22	para DDNC	AM1	$(\Delta H_f^0)_{T1S}$	σ^+	-1.45 ± 0.13	-29.06 ± 0.22	12	0.964
23	para DDNC	PM3	$(\Delta H_f^0)_{T1S}$	σ^+	-1.50 ± 0.12	-31.72 ± 0.21	12	0.972
24	para DDNC	AM1	$(\Delta H_f^0)_{T2S}$	σ^+	-1.63 ± 0.19	-8.07 ± 0.35	12	0.938
25	para DDNC	PM3	$(\Delta H_f^0)_{T2S}$	σ^+	-1.69 ± 0.20	-12.05 ± 0.37	12	0.935
26	para DDNC	AM1	$(\Delta H_f^0)_{2S}$	σ^+	-2.30 ± 0.21	0.34 ± 0.37	11	0.965
27	para DDNC	PM3	$(\Delta H_f^0)_{2S}$	σ^+	-2.40 ± 0.31	0.28 ± 0.55	11	0.933
28 ^a	para DDNC	AM1	$qC:s$	σ^+	1.52 ± 0.13	-3.30 ± 0.22	10	0.972
29 ^a	para DDNC	PM3	$qC:s$	σ^+	1.73 ± 0.15	-0.62 ± 0.27	10	0.971
30 ^a	para DDNC	AM1	$qC:\tau_1$		0.67 ± 0.10	-8.09 ± 0.17	12	0.900
31 ^a	para DDNC	PM3	$qC:\tau_1$		0.59 ± 0.10	-7.70 ± 0.17	12	0.878
32 ^b	para PC	Exp.	$\log k_i/k_a$	σ^+	-0.75	—	7	0.970
33 ^c	para DDNC	Exp.	$-\log K$	σ^+	-0.84	—	5	0.998

^aThe real numbers are 100 times smaller.

^bSee reference 5a.

^cSee reference 6.

trols its chemical behavior.⁹ Experimental determination and semiempirically calculated results of aryl-substituted carbenes contained in five- or six-membered rings indicated quite clearly that the trend in the sign and in the magnitude of $(\Delta H_f^0)_{TS}$ is largely dependent on the electronic properties of the substituent.^{9,16} Since these studies were concentrated in a limited number of substituents,¹⁶ we investigated the effect of a wide variety of substituents on $(\Delta H_f^0)_{TS}$ of PC and DDNC carbenes. The results shown in Tables I and VI (see $(\Delta H_f^0)_{T1S}$ and $(\Delta H_f^0)_{T2S}$ values) and summarized in Table VIII (entries 1–6 and 22–25) indicate that the singlet-triplet gaps [$(\Delta H_f^0)_{T1S}$ or $(\Delta H_f^0)_{T2S}$] vary from derivative to derivative in quantitative, systematic, and predictable fashion. The values of either $(\Delta H_f^0)_{T1S}$ or $(\Delta H_f^0)_{T2S}$ decrease as the substituents change from electron-donating to electron-withdrawing groups.

In order to gain further information on the decomposition of the substituent effect into the effect on the singlet and triplet carbenes, we compared the ρ_{calc} values of the singlet-triplet gaps, $(\Delta H_f^0)_{T1S}$ and $(\Delta H_f^0)_{T2S}$ (entries 4–6 and 24–25 in Table VIII) with those of the energy differences, $(\Delta H_r^0)_{1S}$ and $(\Delta H_r^0)_{2S}$ (entries 7–9 and 26–27 in Table VIII). The comparison indicates that in all the cases studied the ρ_{calc} values for the singlet-triplet gaps are higher than those of the energy differences. This means that the effect of the substituent on the triplets and on the singlets is reciprocal. In other words, electron-donating groups such as *p*-OH and *p*-NH₂ are singlet stabilizing and triplet destabilizing. This conclusion is confirmed by the atomic charges, qC_{T1} , listed in Tables IV and VII, which show that the negative charge on the carbenic center of a triplet is decreased as the substituent changes from electron-donating to electron-withdrawing groups. These results are in a good agreement with the finding that Π donors stabilize the singlets of substituted methylenes more than the triplets, whereas Π acceptors have the opposite effect.³² In order to establish further credence to the reliability of this computational study, the calculated ρ values of the differential energies for processes 1S, $(\Delta H_r^0)_{1S}$ (entries 7–9 in Table VIII), and 2S, $(\Delta H_r^0)_{2S}$ (entries 26–27 in Table VIII), were compared with those of experimental values (entries 32–33 in Table VIII).^{5a,6} The comparison of the results shows a good agreement among the semiempirical and experimental methods. Also, it is noteworthy that the difference between the calculated ρ values for processes 1S and 2S (–2.83 to –4.38 and –2.3 to –2.4, respectively) and the solution kinetic values for pyrolysis of rigid aryl-substituted diazomethanes ($\rho = -0.84$)⁶ and photolysis of substituted phenylcarbenes ($\rho = -0.75$)^{5a} is likely the result of both solvent participation and the only incipient development of the substituent effects in the activated complexes at the transition states of the dissociation reactions in solvent.

Examination of the singlet-triplet gap values, $(\Delta H_f^0)_{T1S}$ and $(\Delta H_f^0)_{T2S}$ (Tables I and VI), indicates that in all the cases studied the triplets are more stable than the singlets (the magnitude of the difference is dependent on the calculation method).³³ On the basis of this result, one might expect that these arylcarbenes would react mainly in the triplet states. However, the experimental data show that these carbenes react mainly in the singlet states.^{5a,6} The discrepancy between theory and experiment exists chiefly because the reaction of the photochemically generated singlet carbene is substantially faster than the competing intersystem crossing processes.^{5a,6}

The comparison between the calculated properties of the nonrigid phenyl (PC) and the rigid (DDNC) systems indicates that in both systems the effect of the substituents is similar. Electron-donating groups stabilize the singlets with concomitant destabilization of the corresponding triplets, whereas electron-withdrawing groups have the opposite effect. Moreover, the difference between the ρ_{calc} values of the differential energies for process 1S, $(\Delta H_r^0)_{1S}$, and those for process 2S, $(\Delta H_r^0)_{2S}$, (entries 7–9 vs. 26–27 in Table VIII) is perhaps related to the effect of the allylic bond in stabilizing the singlet of DDNC carbenes. This is analogous to what has been seen in aromatic carbocations.^{20b,34}

The magnitude of the singlet-triplet gaps is directly related to the energy difference between the *p* and σ nonbonding orbitals of the carbene. Since this energy difference, in part, is affected by the carbon-carbon bond angle, it might be expected that the magnitude of the difference between the bond angles of the triplet and the corresponding singlet would be a good index in determining the magnitude of the singlet-triplet gap.^{9,16} Examination of Tables III and VII indicates that the difference between the bond angles of the triplet and the corresponding singlet of DDNC carbenes is about 15° (Table VII), whereas that in the PC system is about 40° (Table III). This result suggests that the singlet-triplet gap in the PC system should be much higher than that of the DDNC system. As expected, a brief inspection of Tables I and VI, reveals that the magnitudes of the singlet-triplet gaps for DDNC carbenes are much smaller than those of the PC carbenes (compare the values of either $(\Delta H_f^0)_{T1S}$ or $(\Delta H_f^0)_{T2S}$ in Table I to those in Table VI).

CONCLUSION

We have reported a systematic semiempirical study on the relationship between structure and reactivity of substituted rigid and nonrigid arylcarbenes. The value of the quantitative application of these semiempirical methods, in particular AM1 and PM3, outlined in this paper is that it provides a rationale for predicting the effect of substituents on the proper-

ties of aromatic carbenes. In the absence of enough experimental measurements of singlet-triplet gaps of arylcarbenes, it is reasonable to hope that these methods will provide an efficient guide to predict selectivity and reactivity as well as intersystem crossing for a wide variety of arylcarbenes.

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