(M^+ − 4 Cl), 440 (M^+ − 6 Cl), 403 (M^+ − C_6Cl_5). (b) A complex mixture (0.045 g) containing some fluorenyl radical **15** (IR spectrum).

Perchloro-4-(phenyl(4-pyridyl)methylene)cyclohexa-2,5-dienone (17). A mixture of radical **13** (0.414 g) and 30% oleum (20 mL) was stirred (23 h) at room temperature and in the dark. The resulting mixture was poured into ice–water and extracted with ether–$CHCl_3$. The resulting solution was dried and evaporated to a residue, which by chromatography through silica gel (CCl_4) yielded starting radical **13** (0.160 g; 39%) and dienone **17** (0.221 g; 55%): orange crystals, mp 288–290 °C; IR (KBr) 1652 (s), 1551 (m), 1508 (s), 1470 (m), 1350 (m), 1330 (s), 1305 (s), 1252 (m), 1218 (m), 1195 (m), 1127 (s), 1008 (s), 852 (m), 765 (m), 750 (s), 730 (s), 718 (m), 670 (s), 647 (m), 628 (m), 521 (m), 502 (m) cm^{-1}; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{13}NO$: C, 30.6; Cl, 65.2; N, 2.0. Found: C, 30.9; Cl, 65.2; N, 2.2.

Perchloro-9-(4-pyridyl)fluoren-3-one (18). A mixture of radical **15** (0.060 g) and 30% oleum (10 mL) was treated as in the preceding reaction, yielding fluorenone **18** (0.042 g; 72%): red crystals, mp over 350 °C; IR (KBr) 1652 (s), 1572 (m), 1520 (s), 1392 (m), 1370 (m), 1360 (m), 1318 (s), 1303 (m), 1210 (m), 1182 (m), 1157 (m), 1120 (m), 1030 (m), 1013 (s), 960 (m), 921 (m), 853 (m), 820 (m), 780 (m), 761 (m), 730 (m), 683 (m), 645 (m), 503 (m) cm^{-1}; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{11}NO$: C, 34.0; Cl, 61.3; N, 2.2. Found: C, 34.0; Cl, 61.2; N, 2.2.

Perchloro-9-phenylindeno[2,1-*b*]pyridin-3-one (22). A mixture of radical **14** (0.100 g) and concentrated H_2SO_4 (10 mL) was stirred (2 days) at room temperature and in the dark. The resulting mixture was treated as in the preceding reaction, and the residue yielded, by column chromatography (silica gel), indole **9** (elution with hexane) (0.046 g; 48%) and ketone **22** (elution with $CHCl_3$) (0.025 g; 28%): red crystals, mp over 325 °C; IR (KBr) 1697 (s), 1642 (s), 1593 (m), 1522 (m), 1348 (s), 1298 (m), 1152 (m), 1090 (m), 1034 (m), 953 (m), 823 (m), 747 (m) cm^{-1}; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{11}NO$: C, 34.0; Cl, 61.3; N, 2.2. Found: C, 33.8; Cl, 61.1; N, 2.1.

Perchloro-2-(diphenylmethylene)pyridin-5(2*H*)-one (19). A mixture of radical **14** (0.081 g) and concentrated HNO_3 (10 mL) was stirred (2 days) at room temperature and in the dark. The resulting mixture was poured into ice–water and extracted with CCl_4. The organic extract was washed with water, dried, and evaporated to give a residue, which by TLC (silica gel; CCl_4–hexane) gave dienone **19** (0.075 g; 95%): orange crystals, mp 246–248 °C; IR (KBr) 1688 (s), 1593 (m), 1538 (m), 1346 (m), 1332 (s), 1310 (m), 1260 (m), 1102 (s), 1022 (m), 821 (m), 790 (m), 776 (m), 759 (m), 680 (m), 658 (m), 650 (m), 547 (m) cm^{-1}; UV-vis ($CHCl_3$), Table I of supplementary material. Anal. Calcd for $C_{18}Cl_{13}NO$: C, 30.6; Cl, 65.2; N, 2.0. Found: C, 30.7; Cl, 65.2; N, 2.0.

Acknowledgment. We thank Dr. J. Rivera for the mass spectra and Dr. J. Olivella for spin-density calculations on protonated and nonprotonated 4-pyridylmethyl radical.

Supplementary Material Available: UV spectra and magnetic susceptibility data of radicals **13**–**16** and UV spectra of ketones **17**–**19** and **22** (4 pages). Ordering information is given on any current masthead page.

Semiempirical Calculations of Carbenes with Aromatic Substituents: A Comparison of Theory with Experiment

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MINDO/3, MNDO, and AM1 calculations were carried out on a set of 20 singlet and triplet carbenes with aromatic substituents. The computational results were compared with experimental determinations of the structure, energy, and reactivity for those cases where these parameters have been determined. The three semiempirical methods yield comparable results; each gives essentially the same geometry and consistently predicts the energy difference between the triplet and singlet states (ΔH_{st}) of aryl-substituted carbenes contained in five- or six-membered rings. The calculations give values of ΔH_{st} that are approximately linearly related to the experimental estimates of the energy gap. The trend in ΔH_{st} is related to electronic properties of the substituent and the bond angle at the carbene–carbon. The predicted values of ΔH_{st} from the MINDO/3 method are uniformly closer to the experimental values than are those of MNDO or AM1. The electrophilic reactivity of these singlet carbenes is found to be related to their calculated LUMO energies.

One objective of chemical research is to relate systematically and reliably the structure of a substance to its chemical and physical properties. Attaining this objective requires the careful interplay of experiment with theory. It seems unlikely that a more striking example of this interplay than methylene (CH_2:, the simplest carbene) will be found. The long history of this pursuit has recently been described by Schaefer and Shavitt.[1] There were two contentious issues; the bond angle of triplet ground-state methylene and the energy gap (ΔH_{st}) between the triplet and the lowest singlet state of this molecule. Presently theory and experiment[2] are in agreement; the triplet is bent (134°) and 8.5 kcal/mol below the singlet state. After throughtful consideration of methylene and other cases, Schaefer ends his review with the conclusion that quantum chemistry is coming of age as a full partner with experiment.

Research on carbenes entered a new phase in 1976 when Closs and Rabinow reported the detection and characterization of diphenylmethylene (DPM) by flash photolysis of diphenyldiazomethane in solution.[3] Their kinetic

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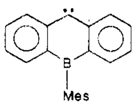
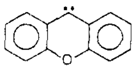
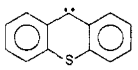
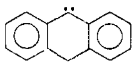
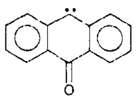
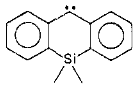
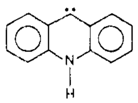
(1) (a) Schaefer, H. F., III. *Science (Washington, D.C.)* **1986**, *231*, 1100. (b) Shavitt, I. *Tetrahedron* **1985**, *41*, 1531.

(2) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

(3) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

Table I. Carbenes in Six-Membered Rings

		triplet				singlet			ΔH_{st}, kcal/mol			
	symbol	θ, deg	SOMO1, -eV	SOMO2, -eV	ΔH_f, kcal/mol	θ, deg	LUMO, -eV	ΔH_f, kcal/mol	MINDO/3	MINDO	AM1	exptl
	BA	137	4.05	3.91	129.5	120	1.22	137.1	7.6	15.5		4.6[a]
	XA	128	3.97	3.23	74.4	114	0.30	67.8	−6.6	2.2	−3.5	≤−5.7[b]
	TA	138	3.88	3.54	120.3	122	0.64	122.2	1.9	8.2	2.8	+[c]
	AN	133	3.93	3.64	133.6	118	0.73	137.2	3.6	8.6		+
	ANO	133	4.24	4.25	99.8	118	1.23	107.5	7.7	13.0		5.1[d]
	SI	141	3.82	3.70	82.6	125	0.76	90.0	7.4	15.5		+[e]
	AC	131	3.91	3.07	119.5	116	0.17	110.2	−9.3			?[f]

[a] Lapin, S. C.; Bauer, B.-E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092. [b] Reference 21. [c] + indicates the sign of ΔG_{st} determined by ESR spectroscopy; ref 19. [d] Devolder, P.; Bourlet, P.; Dupert, C.; Dessaux, O. *Chem. Phys. Lett.* **1972**, *14*, 57. Field, K. W.; Schuster, G. B. *J. Org. Chem.*, submitted for publication. [e] Sekiguchi, A.; Ando, W.; Sugawara, T.; Iwamura, H.; Liu, M. T. H. *Tetrahedron Lett.* **1982**, 4095. [f] Carbene has not been prepared.

measurements indicated that the energy gap separating the triplet from the lowest energy singlet state in this case was ca. 3 kcal/mol. Since this pioneering experiment, related time-resolved laser spectrophotometric measurements on other aryl-substituted carbenes have been carried out.[4] These experiments have shown that ΔH_{st} is a sensitive function of the structure of the carbene and that the magnitude of this gap largely determines the chemical properties of these species.

Unfortunately, it is not practical to apply the elegant ab initio theoretical techniques described by Schaefer to aryl-substituted carbenes. Even the simplest case, phenylmethylene, is too large to handle completely with current computational and financial constraints. This situation has led to sporadic attempts to apply semiempirical theory to these compounds. The first thorough analysis of this problem appeared in the 1968 report of Hoffmann and co-workers who applied extended Hückel theory to phenylmethylene (PhCH:, PM) and DPM.[5] Extended Hückel calculations do not take account of electron–electron interactions, and this early attempt could only provide rough empirical criteria for deciding the ground-state spin multiplicity of the carbenes. However, this report provided an important framework for considering the effect of aryl substituents on the chemical and physical properties of carbenes. In a subsequent paper, Gleiter and Hoffmann provided a prophetic recipe for stabilizing singlet carbenes and inverting their normal order of triplet below singlet state.[6]

There appears to have been some reluctance to apply semiempirical theory to the study of carbenes. Perhaps this was a consequence of the well-known poor agreement initially encountered between experiment and the high-level theoretical approaches used for methylene itself. In an early effort, Dewar and co-workers applied MINDO/2 to methylene and some simply substituted methylenes; they concluded that the ground states of these molecules are triplets.[7] Later, Metcalfe and Halevi carried out INDO calculations on DPM and on fluorenylidene (FL).[8] Their results indicated that ΔH_{st} of the former was ca. 3 kcal/mol, in reasonable agreement with current experimental estimates,[9] but that triplet FL was 21 kcal/mol below its singlet. Experimental measurements of ΔH_{st} for FL give a value of ca. 2 kcal/mol.[10] Dürr and co-workers report extended Hückel calculations on benzocyclobutenylidene and concluded, qualitatively, that the ground state was a triplet.[11] EHT calculations from this group also indicated that both xanthenylidene (XA) and thiaxanthenylidene (TA) have triplet ground states.[12]

We report herein the results of semiempirical calculations on aryl carbenes. Many of the structures examined were chosen because experimental estimates for ΔH_{st} are available and thus the validity of the calculations may be judged. The findings show that MINDO/3,[13] MNDO,[14] and AMI[15] give essentially the same geometries and, with

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[4] Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311.

[5] Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

[6] Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.

[7] Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

[8] Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 634.

[9] Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science (Washington, D.C.)* **1984**, *225*, 1439.

[10] Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833. Griller, D.; Hadel, L.; Nazran, A. S.; Platz, M. S.; Wong, P. C.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2227.

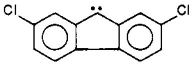
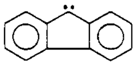
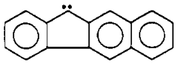
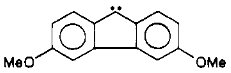
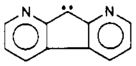
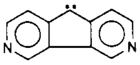
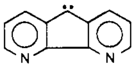
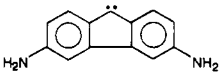
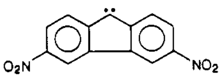
[11] Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, M., Jr. *J. Org. Chem.* **1980**, *45*, 973.

[12] Dürr, H.; Fröhlich, S.; Kausch, M. *Tetrahedron Lett.* **1977**, 1767.

[13] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

[14] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

Table II. Carbenes in Five-Membered Rings

		triplet				singlet			ΔH_{st}, kcal/mol			
	symbol	θ, deg	SOMO1, –eV	SOMO2, –eV	ΔH_f, kcal/mol	θ, deg	LUMO, –eV	ΔH_f, kcal/mol	MINDO/3	MNDO	AM1	exptl
	DCFL	117	4.61	4.39	137.1	104	1.34	141.7	4.6	6.5	0.4	3.6[a]
	FL	117	4.11	3.90	152.1	104	0.86	156.1	4.0	5.1	0.3	1.3[b]
	BFL	114	4.10	3.81	179.6	101	0.84	180.8	1.2	3.3	–2.4	0.4[c]
	DMFL	118	3.96	3.53	58.2	105	0.58	57.4	–0.8	3.1	–2.1	∼–2.7[d]
	18FL	115	4.25	4.13	154.6	102	1.05	157.3	2.7	8.9	3.5	+[e]
	36FL	117	4.20	4.11	163.5	104	0.98	169.8	6.3	7.8	2.1	+[f]
	45FL	117	3.88	3.75	150.9	104	0.79	153.1	2.2	4.3	–1.0	?[g]
	DAFL	117	3.66	3.18	131.0	105	0.32	129.7	–1.3			?
	DNFL	117	5.19	5.07	114.6	104	2.21	129.0	14.4			?

[a] Rak, S.; Lapin, S.; Falvey, D. E.; Schuster, G. B. *J.* Am. *Chem. Soc.* **1987**, *109.* [b] Reference 10. [c] Grasse, P.; Zupancic, J.; Lapin, S.; Hendrich, M.; Schuster, G. B. *J. Org. Chem.* **1985**, *50*, 2352. [d] Chuang, C.; Lapin, S.; Schrock, A.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4238. [e] + indicates the sign of ΔG_{st} determined by ESR spectroscopy; ref 24. [f] Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 4460. [g] Carbene has not been reported.

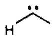
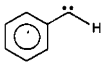
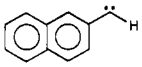
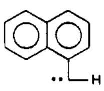
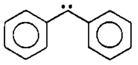
certain limitations, reasonable estimates of ΔH_{st}. The calculations offer a reliable guide to the prediction of the chemical and physical properties of aryl-substituted carbenes.

Results and Discussion

The carbenes selected for examination are distributed among three groups. Those in Table I contain the carbene carbon in a six-membered ring "fused" to two aryl "substituents". The carbenes in Table II are in analogous five-membered rings, and those in Table III have aryl substituents (except for methylene itself) but are not constrained geometrically by incorporation in a ring.

The structures and energies of the carbenes listed in Tables I–III were calculated by the MINDO/3, MNDO, and AM1 methods developed by Dewar and co-workers contained in the AMPAC family of programs.[16] Geometries were fuly optimized for both the singlet and the triplet states. The energies for the open-shell triplets were calculated by the recommended RHF, half-electron approximation method at the UHF geometry.[17] The energies for the singlet states were calculated also with the RHF approximation but without configuration interaction (CI). We found by examination of a few examples that the inclusion of configuration interaction merely lowers the calculated energies of all the singlet carbenes uniformly by ca. 0.5 (2 × 2) and 1.0 (4 × 4) kcal/mol but, of course, requires much more computational time.

Table III. Miscellaneous Carbenes

		ΔH_{st}, kcal/mol			
	Symbol	MNDO	MINDO/3	AM1	exptl
	CH_2	30.1	8.7	30.1	8.5[a]
	PH	19.2	2.2		+[b]
	2NA	18.1	1.1	13.5	+[b]
	1NA	17.7	2.5		+[b]
	DPM	13.0	8.8		2.6[c]

[a] Reference 2. [b] Reference 19. [c] Reference 9.

The restrictions imposed by the rigid nature of the carbenes listed in Tables I and II limit the range of acceptable structures and permits the separation of electronic and geometrical perturbations to their properties. Not surprisingly, the calculations indicate that these carbenes are planar. The carbene–carbon bond angles vary from structure to structure in a systematic and predictable fashion. This angle is smaller for the singlet of each carbene than it is for the triplet. For example, the calculated angle for singlet FL is 104°, and in the triplet this angle increases to 116°. Also, the bond angles in the six-membered ring cases increase approximately with the bond distances to the atom in the 10-position. The size of the carbene–carbon bond angle, in part, determines the magnitude of ΔH_{st}.

It is important in the evaluation of the reliability of these calculations to compare the predictions with available experimental findings. It is understood and widely accepted that the bond angle in triplet methylene is larger than it is in the singlet. This pattern is expected to be

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(15) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898.
(16) Available from QCEP, Bloomington, Indiana.
(17) Clark, T. *A Handbook of Computational Chemistry*; Wiley: New York, 1985; Chapter 4.

repeated throughout this entire class of compounds and is seen in the results of the calculations. There are only two instances where experimentally supported geometries are available for aryl-substituted carbenes.[18] Magnetic resonance spectra of DPM and FL were recorded and interpreted to show that the carbene–carbon bond angle of ^{3}FL is between 105° and 116° and that for ^{3}DPM the two benzene rings are not coplanar (dihedral angle of 36°) and have a carbene bond angle of 149°. The calculations are in substantial agreement with the experimental measurements for FL.

The energy difference between the singlet and triplet state of a carbene in large part controls its chemical behavior.[4] Estimates of this quantity were obtained from the calculations by subtracting the heat of formation of the triplet carbene from that for the singlet at their respective equilibrium geometries. As defined, this quantity is positive when the triplet is the ground state and negative when the singlet carbene is lower energy than the triplet. Inspection of Tables I and II reveals systematic changes in ΔH_{st} and a zero-crossing (switch from triplet to singlet ground state) for both sets.

The most sensitive test of the validity of these calculations comes from comparison of the experimental values for ΔH_{st} with the predicted values. It is important in the evaluation of this comparison to understand the limitations on both groups of numbers. The experimental determinations of ΔH_{st} rest on two sorts of experiments; the first gives only the sign of this quantity, but the second is capable of providing its magnitude.

ESR spectroscopy has been employed with regularity to show that the ground states of most aryl carbenes are triplets (ΔG_{st} = +), but in no case has it been possible to obtain the magnitude of the energy difference between a singlet and triplet carbene from an ESR experiment.[19] Estimates of the magnitude of ΔG_{st} have been obtained experimentally from kinetic measurements.[4] Fundamentally, the rate of interconversion of the singlet and triplet carbenes (k_{st} and k_{ts}) are determined (sometimes indirectly) by laser spectroscopy. The ratio of these rate constants gives K_{st}, the equilibrium constant connecting the singlet and triplet carbenes, and hence ΔG_{st} (conversion from ΔG to ΔH is made by assuming that the entropy difference is entirely a result of their being three triplet components and only one singlet state). It is important to recognize that interpretation of the kinetic experiments requires the assumption of a reaction mechanism. In some cases, the assigned mechanism has been challenged, and the derived value of ΔH_{st} may be viewed as controversial.[20] However, the kinetic experiments do, at the very least, provide a convenient way to rank the magnitudes of ΔH_{st} for a variety of carbenes even if the absolute values of ΔH_{st} remain somewhat uncertain.

The calculations and the ESR spectroscopic results are in perfect agreement. A triplet ground state is predicted in each case where characteristic ESR spectra for the carbene have been observed. Experimental estimates of ΔH_{st} are available for seven of the carbenes listed in Tables I and II. Comparison of these with the calculated values reveals an identical ordering for the energy gaps. The MNDO calculations consistently give values for ΔH_{st} larger than those obtained experimentally,[21] and AM1 gives smaller estimates, but the MINDO/3 results agree remarkably well with the experimental results. This is seen from inspection of Figure 1, a plot of the experimental energy gaps against the values calculated with MINDO/3.

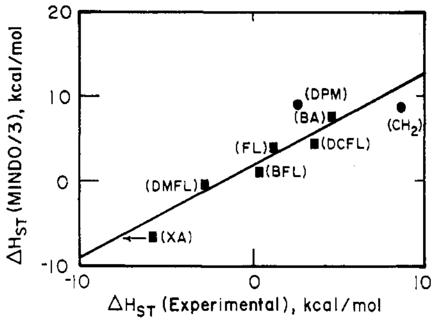

Figure 1. Plot of calculated singlet–triplet gap against experimentally determined values. The squares are carbenes constrained to five- and six-membered rings, the circles to unconstrained examples (see tables for identification of the carbenes). The experimental value for XA is an upper limit; movement in the allowed direction of the indicated arrow will improve its agreement with the other examples. The line is the least-squares fit to the square points.

The experimental energy gaps for methylene and DPM do not agree well with the predictions from the MNDO or AM1 calculations. MINDO/3 comes close to the experimental value for methylene, but for DPM it, too, is well off the mark. It is apparent that the good correspondence found for the carbenes of Tables I and II breaks down in this case. This is a result of the inability of the semiempirical method to compute the structure of this carbene accurately. The MNDO calculations predict a dihedral angle of ca. 1° and a bond angle of 173° for the triplet—far away from the structure indicated by the magnetic resonance experiments. Fixing the structures of both singlet and triplet DPM at the experimental triplet geometry gives ΔH_{st} = 1.0 kcal/mol. Decreasing the bond angle of the singlet at constant dihedral angle to values below the optimized value (159°) increases this gap as expected. Unfortunately, these calculations on DPM cannot be compared with experiment because the structure of the singlet carbene has not been determined.

The lack of experimental data for the "noncyclic" carbenes of Table III do not permit critical evaluation of the calculations for this class. However, the reliable prediction of the relative values for ΔH_{st} and the reasonable correlation revealed in Figure 1 substantiate the predictive power of the semiempirical method for the structurally restricted carbenes of Tables I and II. It is informative to examine the trends revealed in these calculations in more detail. Two points of interest are how the "aryl substituents" influence ΔH_{st} and how they control the reactivity of the carbene.

In most cases the effect of the aryl substituent on ΔH_{st} can be related qualitatively to the relative response of the two singly occupied orbitals of the triplet carbene. In this scheme the substituents are classified first by their effect on the bond angle and then as being π-donating or -accepting and as σ-donating or -accepting with respect to a hydrocarbon standard. For example, anthracenylidene (AN) is chosen as the standard for the carbenes in Table I (FL for those in Table II). Conversion of AN to xanthenylidene (XA) is accomplished conceptually by

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(19) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1975; p 185.

(20) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(21) Dewar and co-workers have also observed that MNDO underestimates triplet energies: Dewar, M. J. S.; Fox, M. A.; Campbell, K. A.; Chen, C.-C.; Friedheim, J. E.; Holloway, M. K.; Kim, S. C.; Liescheski, P. B.; Pakiari, A. M.; Tien, T.-P.; Zoebisch, E. G. *J. Comput. Chem.* **1984**, *5*, 480.

changing the methylene group at the 10-position in the former to an oxygen atom in the latter. This substitution decreases the bond angle and thus increases the s-character in SOMO1 (the singly occupied orbital or σ-symmetry) concomitantly lowering its energy. Also, relative to the electronic properties of the methylene group of the standard, the oxygen is π-donating and σ-accepting. Thus, as expected, the energy of SOMO2 (the singly occupied orbital of π-symmetry) is pushed higher by π-donating oxygen. SOMO1 is also expected to move lower in response to σ-electron withdrawal, but this cannot be easily separated from movement in the same direction in response to the bond-angle change. The net result is that the energy difference between the two singly occupied orbitals of XA is greater than it is in AN (SOMO1 comes down, SOMO2 goes up). The larger energy difference between these orbitals translates into a smaller value for ΔH_{st} in XA than an AN since promotion of an electron from SOMO1 to SOMO2 will require more energy in XA than it does in AN. In this particular case, the energy difference between SOMO1 and SOMO2 is large enough that the singlet carbene is the ground state (ΔH_{st} is negative according to both calculation and experiment).[22] The opposite electronic effects are seen in the calculations for 10,10-dimethylsilaanthranylidene (SI). In this case the energy of SOMO1 moves up due to the σ-donating silyl group and SOMO2 moves down in response to π-withdrawal.[23] The net result is to bring the singly occupied orbitals closer together and thereby increase the singlet–triplet gap of SI relative to the standard. This qualitative assessment of the substituent effects gives reliable predictions for each of the carbenes in Tables I and II except for BA. In this case SOMO1 moves to lower energy despite prediction of a larger bond angle and expected σ-donation by the boron.[23] However, it has been noted that MINDO/3 parametization for boron is suspect.[17]

It is interesting to compare thiaanthrylidene (TA) with XA. Experiments reveal and the calculations concur that the ground state of TA remains a triplet.[24] Comparison of the SOMO energies of XA and TA shows that this switch is primarily a consequence of SOMO2 in TA not moving as high in energy as the corresponding orbital in XA. Thus, within the model described above, sulfur is not as good a π-donor as is oxygen. This may reflect less effective overlap of sulfur's donor 3p orbitals with the carbon 2p orbitals of the arene.

A second general trend in reactivity that the calculations highlight concerns the relative electrophilicities of the singlet carbenes in Table I and II. For example, experiments have shown that XA is a much less powerful electrophile than FL.[4] Singlet FL successfully inserts into the unactivated C–H bonds of cyclohexane in competition with other reactions of the carbene, but XA gives no C–H insertion at room temperature. On the other hand, singlet 1,8-diazafluorenylidene[25] is such a powerful electrophile that it reacts almost completely indiscriminately, and even intersystem crossing to the ground-state triplet does not compete effectively with its reactions. This trend in electrophilic reactivity is revealed by consideration of the relative energies of the LUMOs of the singlet state carbenes. The lower the calculated energy of this orbital, in general, the greater is the electrophilic reactivity of the singlet carbene.

Conclusions

Semiempirical molecular orbitals calculations give reliable and useful estimates of the properties for a restricted set of carbenes. In particular, the results demonstrate that MINDO/3 calculations provide reasonable estimates of the structure and energies of planar, aryl-substituted carbenes constrained to five- or six-membered rings. In contrast, these semiempirical methods do not give reliable results for DPM, which is not so constrained. These findings should help guide the search for new carbenes with unusual or interesting properties.

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