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A Molecular Orbital Study of Phenylcarbene and Diphenylcarbene

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The potential surfaces of diphenylcarbene and phenylcarbene, in singlet and triplet states, have been studied by using the AM1 molecular orbital method. The triplet was found to be the ground state in both cases. The energy difference between the triplet and singlet surfaces is calculated to be somewhat higher than that required by a mechanism for reaction of triplet I with methanol via a thermally populated singlet state. The electron affinity of I was calculated to be quite large (43.2 kcal/mol), suggesting the possibility of a mechanism involving electron transfer from methanol to I. The characteristics of suberanyl and suberenyl carbenes were calculated for comparison.

The insertion reaction of triplet-state diphenylcarbene, I, into the O–H bond of alcohols (reaction 1) has been a subjectof considerable interest. As triplet carbenes are thought to be inert toward alcohols, several groups have invoked mechanisms in which the (ground) triplet state of I is thermally excited to a singlet state, which, subsequently, inserts into the O–H bond (scheme I).[1] This mechanism has been recently challenged by Griller et al. who reported an activation energy for the reaction which seemed too low to be consistent with the singlet–triplet energy gap.[2] They have suggested the possibility of a reaction emanating directly from the triplet of I.

In this paper, first we examine the potential surfaces for phenylcarbene, diphenylcarbene, and several related carbenes in the lowest triplet and two lowest singlet states to determine the relative energies of the species as a function of geometry and to locate any regions of the (ground) triplet surface where promotion to a singlet might be favorable. Then, we investigate the direct interaction of methanol with several carbenes. While this paper was in preparation, Li and Schuster reported semiempirical calculations on many carbenes, including several treated here. Our results differ somewhat from theirs, as discussed below.[3]

Scheme I

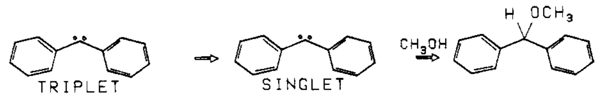

Table I

	heats of formation[a]			
species	triplet	singlet (RHF)	singlet open shell	anion
diphenylcarbene, I	119.2	131.7	128.7	76.0
diphenylmethane		42.8		
phenylcarbene, II	102.9	117.6	114.4	86.1
toluene		14.4		
suberenylcarbene, III	140.1	149.2	148.3	113.6
suberene	139.0	70.7		
suberanylcarbene, IV	115.3	125.1	127.2	89.9
suberane	106.9	41.3		
florenylidene	153.1	153.5	161.9	
methylene	80.8	110.9 105.4[b]	105.9	

[a] All energies are in kilocalories/mole. "Anion" refers to the radical anion formed upon capture of an electron by the corresponding carbene. [b] With CI (2 × 2).

Methods

Molecular orbital calculation were performed by using the AM1 approximation to molecular orbital theory.[4] This method has been shown to provide accuracy similar to that expected from 6-31G* ab initio calculations in the cases where direct comparisons are possible.[5] Both AM1 and the similar MNDO[6] methods have been successfully used to study the reaction path involving species containing unpaired electrons.[7] The geometries of all species were completely optimized with the following exceptions: (a) C_{2S} or C_{2V} symmetry was enforced where appropriate, and (b) the rings of phenyl and diphenylcarbene were kept planar. Reaction paths were calculated by optimizing all parameters other than the reaction coordinate while stepping through a series of fixed values for the latter.

Three energy states were considered for each carbene species: the triplet state, which was calculated using the standard half electron procedure[8] in the AMPAC computer program; and two singlet states, one a RHF closed shell state with all electrons paired and one empty valence orbital; the second, an open shell with one electron in each of two orbitals. The former is obtained by using the standard RHF procedure and the latter by employing 3

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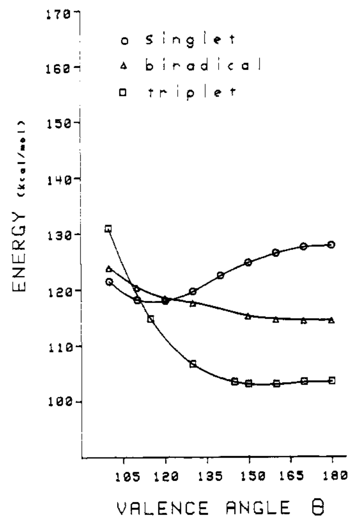


Figure 1. Variation of energy (heat of formation) with valence angle for phenylcarbene.

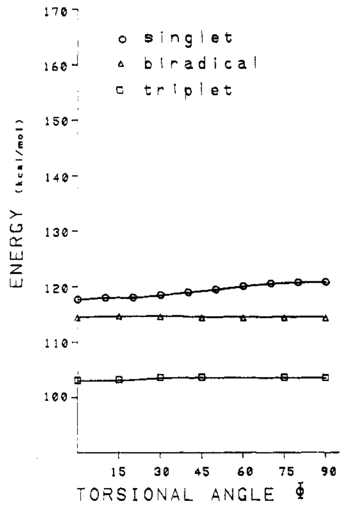


Figure 2. Variation of energy (heat of formation) with torsional angle for phenylcarbene.

× 3 configuration interaction (CI) starting with the self-consistent open-shell orbitals (using the "biradical" keyword in the AMPAC program). The biradical procedure allows the ground singlet states of the carbenes in question to include open-shell (singlet) character. A limitation of this methodology is that the open-shell SCF orbitals used in the biradical procedure are not orthogonal to the SCF ground state orbitals obtained from the standard RHF calculation. Ideally, one would do a multiconfiguration (MCSCF) calculation that would include all of the states that might contribute to the proper description of the carbene. As this is clearly impossible for systems as large as those treated in this study, we have decided to use the procedures indicated above.

Radical anions were calculated using the half-electron method.

Results and Discussion

The energies of the triplet and two singlet states of phenylcarbene were calculated as a function of the valence angle, θ, and the torsional angle, ϕ. The energies are presented in Figures 1 and 2, and Table I. As can be seen from Figure 1, the triplet state is the ground state at values of $\theta > 110°$. The biradical singlet is the lower of the two singlet states for $\theta > 120°$. The global singlet minimum is for this state at $\theta = 180°$. The closed-shell (RHF) singlet has a minimum near $\theta = 115°$, which is slightly higher than overall singlet minimum. The overall energy minimum occurs at about $\theta = 150°$, but the energy is rather insensitive to θ for values above 150°. The effect of changing ϕ upon the energy is small for all three states of phenylcarbene.

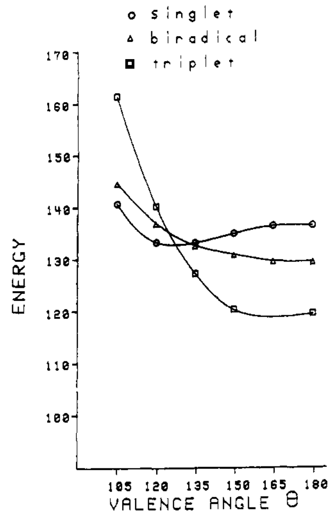


Figure 3. Variation of energy (heat of formation) with valence angle for diphenylcarbene.

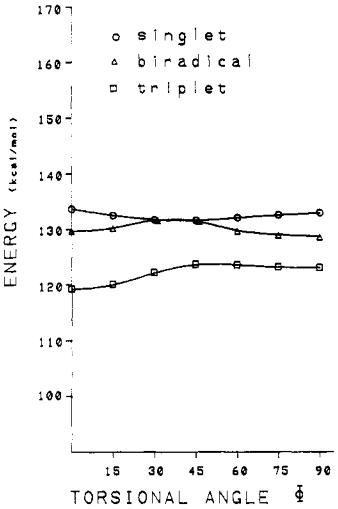
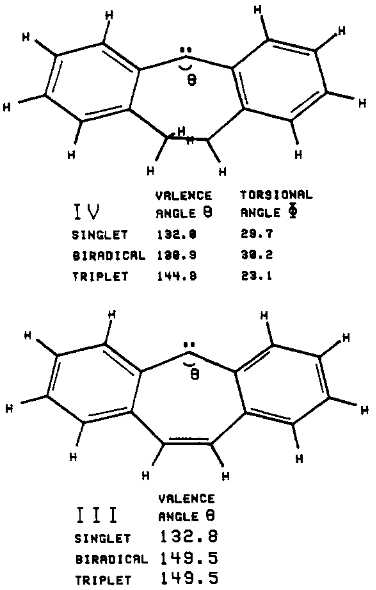


Figure 4. Variation of energy (heat of formation) with torsional angle for diphenylcarbene.

The effects of changing θ and ϕ on diphenylcarbene are qualitatively similar to those found for phenylcarbene (see Figures 3 and 4). The minimum energy for the triplet is at about $\theta = 160°$, but there is little energy difference for θ above 160°. Once again the favored geometry for the biradical state is linear. It is the lower of the two singlet states for $\theta > 130°$, as well as the global singlet state minimum. The RHF, closed-shell singlet has a minimum near $\theta = 120°$, which is only slightly higher in energy than the linear biradical singlet. Again, the energies of all three states are insensitive to the torsional angle, ϕ.

The excitation energy to the singlet state is calculated to be 11.5 kcal/mol for phenylcarbene and 9.5 kcal/mol for diphenylcarbene. There are no obvious regions of the surface for either carbene that would allow for an appreciably lower thermal excitation. Thus, the AM1 calculations predict a singlet-triplet energy separation that is somewhat greater than that required to fit a mechanism for triplet insertion that requires a singlet carbene as an intermediate. One should note that the lower of the two



IV	VALENCE ANGLE θ	TORSIONAL ANGLE Φ
SINGLET	132.0	29.7
BIRADICAL	180.9	30.2
TRIPLET	144.8	23.1

III	VALENCE ANGLE θ
SINGLET	132.8
BIRADICAL	149.5
TRIPLET	149.5

Figure 5. Some geometrical parameters of suberenylcarbene, III, and suberanylcarbene, IV.

singlet states for both I and II is the open-shell state. This state is more geometrically similar to the triplet than that with the nonbonding electrons paired. Excitation to this state from the triplet is more likely to be without activation other than the triplet–singlet energy gap, as the excitation will likely be very close to vertical. Yet, it is the other (closed-shell) state that is thought to react with alcohols by means of an initial (Lewis) acid–base interaction between the empty orbital on the carbene and a lone pair on the alcohol. The corresponding interaction in the open-shell carbene singlet would lead to an initial three-electron bonding interaction that might not be so favorable.

Suberenyl and suberanyl carbenes, III and IV, can be considered as diphenylcarbenes that are forced into geometries with fixed dihedral angles between the rings. The geometrical details are shown in Figure 5. Suberenyl carbene, III, is planar, with valence angles of 133, 150, and 150° at the divalent carbon in the closed- and open-shell singlet and triplet states, respectively. Suberanylcarbene, IV, has corresponding valence angles of 132, 143, and 145° and dihedral angles between the rings of 30, 15, and 23° for the closed- and open-shell singlets and triplet, respectively. These values are in accord with reasonable expectations based upon the variation of the energy of diphenylcarbene with valence and dihedral angles (Figures 3 and 4). The additional double bond in III adds the possibility of conjugation between the rings through the π-bond (in addition to that involving the divalent carbon). The energies of these species were calculated for comparison with I (see Table I). The energy difference between the carbene and the parent hydrocarbon is significantly lower for III than for I or IV. This is apparently due to the interaction of the singly occupied π-orbital with the bonding π-orbital of the extra double bond in III (see Figure 6).

For each of the aromatic carbenes considered, the two singly occupied orbitals in the triplet and open-shell singlet were an orbital localized on the divalent carbon and another delocalized in the π-system. The latter was found to be the higher of the two in all cases. The π-orbital of suberanylcarbene illustrated in Figure 6 is typical for these systems.

The results of the present calculations are in fair to reasonable agreement with INDO calculations reported earlier by Metcalfe and Halevi,[9] in which only the closed-shell singlet was considered. They found the singlet to be only 4 kcal/mol higher than the triplet, in apparent better agreement with the accepted experimental value. However, as has been previously noted by Griller, the energy difference between the lowest singlet and triplet states of I has never been measured directly. In fact, no direct evidence for singlet I has ever been reported. Rather, the energy difference has been estimated from the rates of reaction of triplet I with alcohols. Thus, this value is only reasonable if the thermal excitation to singlet mechanism (Scheme I) is correct.

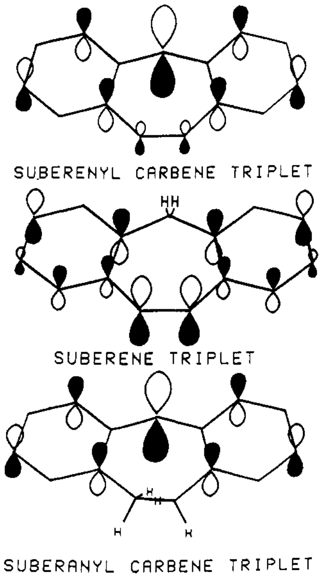


Figure 6. π-SOMO's (single occupied molecular orbitals).

The agreement between the results presented here and those recently reported by Li and Schuster[3] is mixed. They report singlet triplet gaps of 30.1 and 0.3 kcal/mol for methylene and florenylidene, respectively, using AM1. Our result of 24.6 kcal/mol for the singlet–triplet splitting in methylene is due to the inclusion (using 2 × 2 CI) of an important interaction with the doubly excited state. The biradical result for methylene is higher than that of the CI calculation performed with the RHF closed-shell SCF orbitals due to the poorer description of the ground state obtained from the use of the excited-state SCF orbitals. For florenylidene, our value of 0.4 is almost identical to theirs and close to the reported experimental value of 1.1.[10-12] The biradical procedure gives a higher energy, presumably due to the inability of florenylidene (like suberenylcarbene) to widen the valence angle at the divalent carbon. Li and Schuster do not report AM1 singlet–triplet gaps for phenylcarbene or diphenylcarbene. They do report MNDO and MINDO/3 results, which are in disagreement with each other, both in magnitude and trend (19.2 and 2.2 kcal/mol for phenylcarbene and 13.0 and 8.8 for diphenylcarbene, using MNDO and MINDO/3, respectively). Thus MNDO predicts the triplet gap to de-

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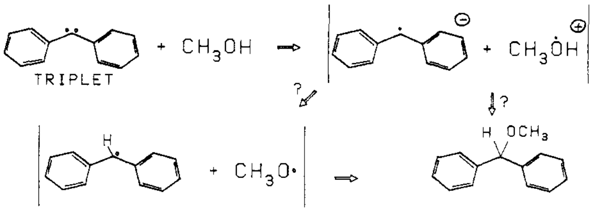
[12] The "experimental" value reported in ref 10 once again employs the assumption that only singlet florenylidene reacts with alcohols. The reasoning may, therefore, be faulty if a mechanism such as that suggested here for diphenylcarbene be operative for florenylidene. Reference 11 reports spectroscopic studies analogous to those of ref 10, without making similar conclusions about the singlet–triplet energy difference.

Table II

species	$E_{st}{}^a$	A^b
diphenylcarbene, I	9.5	43.2
phenylcarbene, II	11.5	16.8
suberenylcarbene, III	8.2	26.5
suberanylcarbene, IV	10.2^c	26.4
florenylidene	0.4^c	
methylene	24.6	
	17.4^d	

[a] All energies in kilocalories/mole. Difference in energy between the triplet and lower of the two single states. [b] Electron affinity. [c] For suberanylcarbene and florenylidene, and RHF singlet was the lower singlet. [d] Corrected for twice the error in the heat of formation of methyl radical (see ref 4).

Scheme II



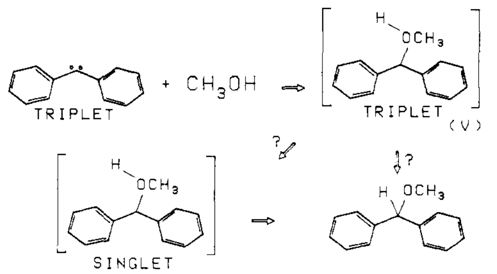
crease upon going from phenylcarbene to diphenylcarbene, while MINDO/3 predicts an increase. The AM1 valence angle (113.8°) for florenylidene triplet is in good agreement with the experimental value (105–116°).[13]

MINDO/3 is not generally considered as a useful method for the calculation of radicaloid species. For example, it predicts the activation enthalpy for H transfer between methyl radicals to be 9.5 kcal/mol. MNDO (which predicts a value of 30.9 kcal/mol for the same activation energy) is generally thought to be better than MINDO/3, but overestimates some repulsions. AM1 correctly predicts the H-transfer activation (15.5 kcal/mol compared to an experimental value of 14.9 kcal/mol).

While AM1 seems to underestimate the heats of formation of simple alkyl radicals, it is substantially more accurate for larger and delocalized radicals, such as benzyl and allyl.[14] To the extent that a methylene triplet might be considered to resemble a double methyl radical, the overestimation of the singlet–triplet gap in methylene might be related to the errors observed for the small alkyl radicals. A corrected value for the methylene singlet–triplet gap is given in Table II. This value represents the calculated value less twice the error in the heat of formation of methyl radical. The calculated splitting (17.4 kcal/mol) is still higher than the experimental value. The good agreement with experiment for the heats of formation of benzyl radical, the singlet–triplet gap and triplet geometry for florenylidene, and the geomtry of triplet diphenylcarbene all suggest that the AM1 calculations on the aromatic carbenes might be considerably more accurate than those for methylene. In the absence of better experimental evidence or calculations of the level necessary to correctly assign the singlet–triplet gap in methylene itself,[15] it is impossible to further qualify the AM1 results.

Since the AM1 results do not lend much support for the mechanism of Scheme I, we considered two other possible reaction paths: (a) a one-electron transfer from methanol to the carbene, followed by H-atom transfer and combination of the radical/ion pair (Scheme II); and (b) direct reaction of methanol with the carbene in its triplet state (Scheme III).

Scheme III



To study the mechanism of Scheme II, we calculated the electron affinities and ionization potentials for the carbenes and methanol, respectively. This was achieved by performing the appropriate fully optimized AM1 calculation on the various radical ions. The electron affinities are obtained as the difference between the energies of the carbene and its respective radical anion. The electron affinity of diphenylcarbene is calculated to be 43.2 kcal/mol (119.2 – 76.0[16] kcal/mol). This value is 26.4 kcal/mol greater than the corresponding value for phenylcarbene. Some of this difference could be ascribed to the greater opportunity for delocalization of the negative charge in the diphenylcarbene rather than phenylcarbene radical anion. However, the electron affinities of both suberanyl and suberenyl carbene, which are similar in size to I, are predicted to be about 17 kcal/mol less than that of I. These results (displayed in Table II) are probably due to the inability of the radical anions of both III and IV to achieve a near linear geometry at the divalent carbon. As can be seen, before correction for the attraction between the ions, the electron transfer is endothermic by 198.9 kcal/mol. Two point charges will have a compensating attraction at a distance of 1.67 Å in a vacuum. It is clearly difficult to estimate the distance at which electron transfer would become exothermic for transfer to more delocalized charges in a complex solution. The endothermicity of the electron transfer (before compensating for the attraction) would be decreased by the aggregate heats of solution of the radical ions. The attraction would be decreased by a factor of $1/\epsilon_s$ (where ϵ_s is the dielectric constant of the solvent). While ionic heats of solution and ϵ_s for bulk solvents can be measured, the relevant values for ions in close proximity, where there may be one or fewer solvent molecules between the ions, is difficult to estimate. Nevertheless, the estimate for the gas phase does indicate that electron transfer may play an important role in the reaction. The observation by Eisenthal that polar solvents tend to decrease the apparent triplet–singlet energy gap[1h] is equivalent to increased rate of reaction of carbene with alcohols in polar solvents. One might expect electron transfer to be favored in polar solvents as increased solvation energies will favor the formation of the intermediate radical ions.

To a certain extent, the mechanism described above might be considered a direct reaction between the triplet carbene and methanol. This would be true if the electron transfer occurred at a short separation of the two species. In such a case, the resulting radical anion/radical cation pair might combine (after an electron spin inversion)

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(16) An experimental value of 81.8 ± 2 kcal/mol has been recently reported for diphenylcarbene radical anion: McDonald, R. M.; Gung, W. Y. *J. Am. Chem. Soc.* **1987**, *109*, 7328.

without activation. Dissociation of the pair would involve reverse electron transfer to regenerate the carbene and alcohol molecules (if it occurred at all). In such a case, no electron-transfer intermediates should be experimentally discernible.

The direct reaction (Scheme III) of methanol with I leads to an intermediate triplet oxygen ylide of structure V. This species is calculated to be 15.8 kcal/mol less stable than the separated species, I and methanol. As a comparison, the corresponding ylide formed from methylene and methanol is predicted to be 1.9 kcal more stable than the separated species. These results suggest that the triplet state oxygen ylide is not an intermediate for this reaction. Turro has reported evidence for the reversible formation of an intermediate, presumed to be an ylide, in the reaction of I with alcohols.[17] It is possible that this intermediate be the radical ion pair of Scheme II.

The most plausible mechanism that does not involve thermal population of the carbene singlet state appears to be the electron-transfer mechanism (Scheme II). This suggestion is consistent with the reports that I reacts with amines[18] and carbon tetrachloride,[19] as one would expect both to participate in electron-transfer reactions at least as well as alcohols. The intervention of the singlet state or an ylide cannot be rigorously ruled out by these calculations. Nevertheless, the activation energies required by the calculated reaction paths for Schemes I and III are beyond the normal errors expected for calculations of the kind presented in this paper.

While it is clear that the calculations reported in this paper cannot approach the level previously achieved for CH_2, they can, nevertheless, provide the insight necessary for designing new and (hopefully) better experiments. In particular, the postulated mechanism can be tested. We do not mean to assert that the calculations prove the mechanism or disprove the suggestion that thermal excitation to the singlet is possible. However, these are the best calculations that can be done currently, and (with appropriate reservations) they certainly do not support the thermal excitation model. We hope these calculations will encourage further thinking in this area.

Acknowledgment. This work was supported in part by grants from the U.S.–Spain Cooperative Research Program, "Comision Asesora de Investigacion Cientifica y Technia" (PB85-0244) and The PSC-BHE.

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Ab Initio Study of the Regiochemistry of Dimetalated Oximes. The Importance of Triple Ions in Isomeric Lithium and Sodium Ion Pairs of the Acetaldoxime Dianion

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The potential energy surfaces of dilithioacetaldoxime and its sodium analogue have been explored at the ab initio level. Several stationary points have been located with a slightly modified 3-21+G basis set. Harmonic vibrational frequencies have been calculated to characterize the stationary points, and energies have been obtained with a slightly modified 6-31+G* basis set. The relative energies of the isomeric dimetalated derivatives of acetaldoxime show a preference for the formation of the syn-configured isomer, whereas in the case of the isolated dianion the anti isomer is thermodynamically favored by 2.2 kcal mol^{-1}. The relative energies of the isomeric metal derivatives of acetaldoxime are in agreement with experiment. The regioselective second deprotonation at the syn α-carbon and the regioselective addition of electrophiles to the syn α-carbon are consistent with the calculated structures of the dimetalated intermediates. These results suggest that these structures of dimetalated oximes be considered in discussions of reaction mechanism. Triple ions formed by the heteroatoms and the cations are the primary structural concept. Chelation by the heteroatoms is more important than the interaction of the cations with the (formally) carbanionic methylene group. The triple ions formed between the heteroatoms and the cations differ in detail due to modes of puckering and give rise to topologically different structures. The syn preference energy for the dilithium derivatives of acetaldoxime is 4.4 kcal mol^{-1}. Sodium increases the syn preference energy to 8.3 kcal mol^{-1} and suggests that larger regioselectivity may be possible by use of bases with large cations. The interactions between sodium and the heteroatoms, nitrogen in particular, are enhanced compared to lithium. Replacement of Li^+ by Na^+ results in structures of different topology in some cases.

Introduction

The regioselective formation of a new CC bond in the α-position of a carbonyl group is one of the fundamental reactions in modern synthetic organic chemistry.[2] Dimetalated oximes[3-12] and a variety of other N derivatives[13] of carbonyl compounds have been successfully employed

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