idal) and C_{2v} (pseudo-trigonal-bipyramidal, with an equatorial nitrido ligand) geometry, as shown in Figure 4 . From an electronic standpoint, this is the geometry that would be expected to result from the weakened OsN π-bonding of the excited state, since this distortion allows one component of d_{xz},d_{yz} (the one unoccupied in the excited state) to be destabilized by increased σ-interaction with the X ligands, while the occupied component is stabilized by decreased σ-interaction. If there were no π-bonding at all, electrostatic considerations would favor a trigonal-pyramidal geometry.

Franck–Condon calculations (employing reported[10] bending force constants and neglecting **F** and **G** matrix mixing) indicate that the b_1 distortion is on the order of 8°, which places the excited-state structure approximately midway between the limiting square-pyramidal and pseudo-trigonal-bipyramidal geometries. That the barrier to this distortion is fairly small for this class of complexes may be inferred from the fact that the valence-isoelectronic species $[ReNCl_2(PPh_3)_2]$ possesses a ground-state geometry[13] very similar to that proposed here for the emissive excited state of $[OsNX_4]^-$.

In support of our interpretation of $[OsNX_4]^-$ excited-state structure, 6-coordinate valence-isoelectronic complexes such as $[ReO_2(CN)_4]^{3-}$ show much smaller distortions along the deformation coordinates, in both absorption and emission, for the analogous electronic transitions.[4] It seems likely to us that the short progressions in low-frequency modes observed for this type of compound[14] represent excited-state Jahn–Teller distortions that are of small magnitude because there is no highly favorable geometry toward which the molecule can distort.

Acknowledgment. M.D.H. thanks the Sun Co. and Standard Oil Co. (Ohio) for providing graduate fellowships. This work was supported by National Science Foundation Grant CHE84-19828 (H.B.G.) and the Caltech President's Fund (V.M.M.). Part of the research included in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Registry No. $[Ph_4As][OsNCl_4]$, 42720-43-4; $[Ph_4As][OsNBr_4]$, 42720-44-5.

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(13) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204–210.

(14) We have also examined two examples of weak axial adducts of $[OsNCl_4]^-$, the compounds $[n\text{-}Pr_4N][OsNCl_4(OH_2)]$ and $K_2[OsNCl_5]$. Luminescence is extremely weak for both even at low temperature, and we have not yet been able to characterize it further.

Structural Control of the Triplet–Singlet Equilibrium in Cyclophane Diarylcarbenes

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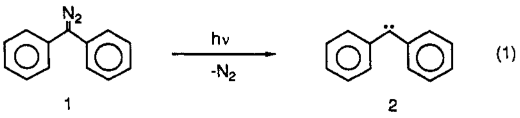
Abstract: The absolute reactivities of [1.*n*]paracyclophane analogues of diphenylcarbene have been investigated by using the technique of laser flash photolysis. The results are consistent with theoretical predictions that the relative stabilities of the triplet and singlet states of these species can be controlled by changing the hybridization at the carbenic center and the torsional angle of the aryl rings.

Significantly different chemical reactivity is observed from singlet and triplet carbenes,[2,3] and thus the relationship between molecular structure and the relative energies of these two states is very important. Of particular interest is the possibility of controlling the relative stabilities of the singlet and triplet states of carbenes, and consequently the reaction products. However, the absolute energy difference between these states has been investigated for very few carbenes. In this regard diphenylcarbene (DPC, **2**) is exceptional in that both the energy difference between the ground triplet and corresponding singlet states ($\Delta E_{ts} = E(\text{triplet}) - E(\text{singlet})$), and the dynamics of their interconversion have been extensively studied.[4,5] This is because the carbene is the archetype arylcarbene and is amenable to time-resolved spectroscopic techniques.[4,5]



Recently the preparation of the [1.*n*]paracyclophane carbenes **4** was reported, together with ESR studies of these species.[6] These carbenes are of significant interest as analogues of diphenylcarbene. Theoretical evidence suggests that for DPC, the energies of the triplet and singlet states depend to differing extents upon the angle (α) between the two aryl carbon–carbenic carbon bonds and the torsional angle (θ) by which the two aryl rings are twisted with respect to a plane defined by the bonds on the carbenic center.[7] It is predicted that the singlet state should be stabilized with respect to the triplet as a function of decreasing α and

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(1) (a) Max-Planck-Institute. (b) Columbia University.

(2) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic: New York, 1971.

(3) *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley Interscience: New York, 1975; Vol. 1 and 2.

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

(5) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

(6) (a) Alt, R.; Staab, H. A. *Tetrahedron Lett.* **1984**, 633. (b) Staab, H. A.; Alt, R. A. *Chem. Ber.* **1984**, *117*, 850.

(7) (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 634.

(8) These results for diphenylcarbene have previously been reported (ref 5).

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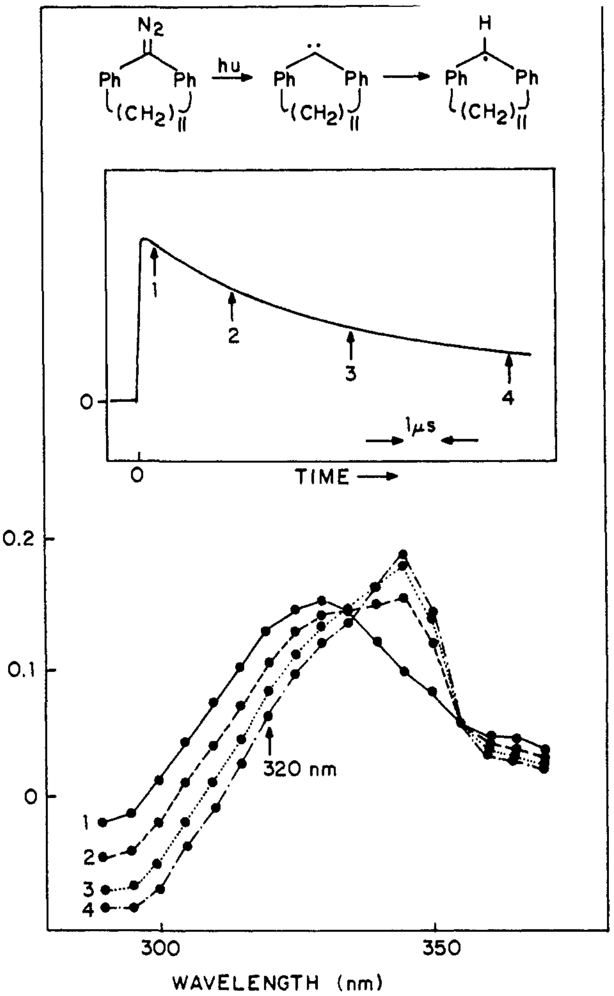
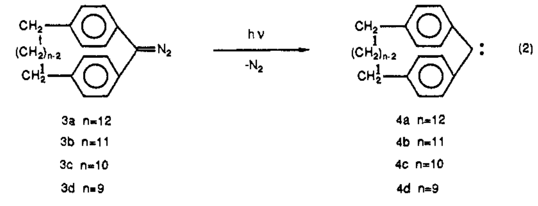


Figure 1. Transient absorption spectra obtained upon laser flash photolysis of diazo compound **4b** in argon-purged hexane. Also shown is the time-resolved behavior observed at 320 nm. The four spectra were recorded at the four times after the laser pulse indicated on the decay trace.

increasing θ. In the carbenes **4**, as a function of decreasing ring size, the aryl rings are twisted with respect to the plane and are increasingly fixed in a position in which θ = 90°. In addition, the angle α becomes progressively smaller with decreasing ring size. Thus we expect that the singlet states of **4** should become stabilized with respect to their triplet states as a function of decreasing ring size (i.e., ΔE_{ts} should decrease). In the present work we present the results of laser flash photolysis studies on the carbenes **4** and provide experimental evidence which supports the theoretical predictions concerning the structural effects on ΔE_{ts}.



(2)

Experimental Section

The [1.*n*]paracyclophane diazo compounds **3** were prepared according to ref 6. Diphenyldiazomethane (**1**) was available from previous studies.[5] The carbene quenchers isoprene (Aldrich Gold Label) and 1,4-cyclohexadiene (Aldrich) were distilled immediately before use. Methanol (MBH Spectrograde), hexane (MBH Spectrograde), and *tert*-butyl alcohol (Fisher) were used as received. Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use.

Solutions of the diazo compounds of ca. 1 × 10^{-3} M were purged with argon prior to analysis by laser flash photolysis. Solutions containing isoprene were purged at 0 °C to prevent evaporation. The flash photolysis apparatus consists of a Lambda Physik Excimer laser (EMG-101, 308 nmn, 20 ns, ca. 40 mj) and a 450W xenon arc used with a PRA 301 power supply and PRA 305 pulser. The transmitted light was passed through an ISA H-10 monochrometer and monitored with an RCA 4840 photomultipler tube which was terminated into 50 Ω. The signal was recorded with a Tektronix 7912AD digitizer which was interfaced to a PDP-11/23 minicomputer.

Table I. Rate Constants (k_q) for Quenching of Diarylcarbenes (M^{-1} s^{-1})[a]

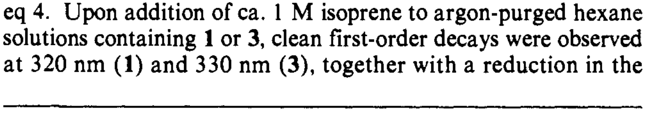
carbene	isoprene[b]	1,4-cyclohexadiene[b]	*tert*-butyl alcohol[c]	methanol[c]
2	1.4 × 10^6	3.4 × 10^6	2.1 × 10^6	6.3 × 10^6
4a	8.6 × 10^6	7.3 × 10^6	8.6 × 10^7	2.0 × 10^8
4b	9.7 × 10^6	7.0 × 10^6	6.0 × 10^7	2.4 × 10^8
4c	1.5 × 10^7	1.2 × 10^7	1.6 × 10^8	6.8 × 10^8
4d	3.8 × 10^7	2.3 × 10^7	7.5 × 10^8	2.0 × 10^9
spread[d]	27	7	350	320

[a] The errors in the rate constants for the isoprene and cyclohexadiene reactions, taken from 2 × standard deviations of the slopes of plots of (k_{obsd}) vs. concentration of quencher (see text), averaged 10%. For the alcohol quenchers similar errors were obtained for the carbenes **4c** and **4d**. For **4a** and **4b** the errors are not known since the corresponding plots were slightly nonlinear (see text and Figure 2). [b] In hexane solvent. [c] In tetrahydrofuran solvent. [d] Rate constant for carbene **4d** divided by rate constant for carbene **2**.

Transient absorption spectra were recorded in a "point-by-point" manner at ca. 5-nm intervals with the monochrometer set at a 4-nm band-pass. Solutions were analyzed on a flow cell to eliminate problems associated with the buildup of products.

Results and Discussion

Flash photolysis of solutions **1** and **3** in argon-purged hexane solvent gave rise to transient absorptions in the region 300–350 nm, although in each case the time evolution of the signal was nonexponential and was dependent upon the monitoring wavelength, which indicated the presence of more than one transient species. Transient absorption spectra showed that as a function of time after the laser pulse, the absorption maxima shifted from shorter (ca. 320 nm) to longer (ca. 340 nm) wavelengths for each diazo compound (for example, Figure 1). Oxygen efficiently quenched the transients formed from all of the diazo compounds. In air-saturated solution, fast exponential decay was observed at 320 nm for **1**, and a 330 nm for **3**, with significant reduction in the longer wavelength absorptions. From the decay rates in air and in oxygen saturated solutions, quenching constants of ca. 2 × 10^9 M^{-1} s^{-1} could be determined in each case for the oxygen quenching of all of the transients. The transients from diazo compound **1** have previously been assigned.[4,5] The decay which is observed at 320 nm and is quenched by oxygen is due to the triplet state of DPC (^{3}DPC), which is formed within the 20-ns laser pulse following loss of nitrogen from **1**, and fast intersystem crossing from the singlet state of DPC. In hydrogen-donating solvents ^{3}DPC abstracts a hydrogen according to eq 3, and the diphenylmethyl radical is formed which has an absorption maximum at 330 nm.[9] By analogy the transient decays which are observed at ca. 330 nm from **3** are assigned to the carbenes **4**, and the longer wavelength absorptions observed at ca. 350 nm are assigned to the corresponding radicals. These assignments are supported by the observed behavior upon addition of other carbene quenchers, which simplify the transient absorptions.



(3)

Isoprene is known to react with diphenylcarbene according to eq 4. Upon addition of ca. 1 M isoprene to argon-purged hexane solutions containing **1** or **3**, clean first-order decays were observed at 320 nm (**1**) and 330 nm (**3**), together with a reduction in the

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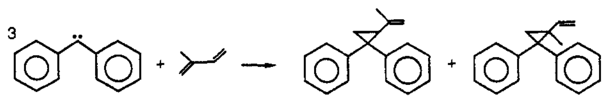
[9] (a) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283. (b) Hadel, L. M.; Platz, M. S.; Wright, B. B.; Scaiano, J. C. *Chem. Phys. Lett.* **1984**, *105*, 539.



(4)

absorptions at 330 nm (**1**) and 350 nm (**3**). Plots of the rate of decay of the absorption at the shorter wavelengths (k_{obsd}) vs. isoprene concentration were linear and gave the quenching constants (k_q) as slopes (Table I).[8] Addition of ca. 1 M 1,4-cyclohexadiene to solutions of **1** or **3** was accompanied by an increase in absorption at 330 nm (**1**) or 350 nm (**3**) so that the time-resolved growth at those wavelengths obscured the decays at shorter wavelengths. Plots of the rate of growth in absorption at 330 nm (**1**) or 350 nm (**3**) vs. 1,4-cyclohexadiene concentration were linear and gave the quenching rate constants given in Table I. 1,4-Cyclohexadiene is known to react with diarylcarbenes by hydrogen abstraction which results in a greater yield of radicals at 330 or 350 nm.[9]

The isoprene- and cyclohexadiene-quenching experiments are entirely consistent with the assignments of the short and long wavelength absorptions to carbenes and radicals, respectively. That each carbene is quenched by oxygen with a rate which is close to one order of magnitude less than the diffusion limit strongly suggests that each is a ground triplet state, like diphenylcarbene. This is, of course, consistent with the observation of ESR signals attributable to triplet carbenes upon irradiation of diazo compounds **3a**, **3b**, and **3d** in low-temperature glasses.[6] However, the result for **4c** suggests that the reason that no ESR signal was observed in this case is not because this carbene is a ground-state singlet.

The absorption maxima of the carbenes in hexane were determined from transient absorption spectra taken immediately after the laser pulse. The absorption maxima of the radicals were obtained from spectra recorded after reaction of the carbenes with the solvent and before complete decay of these species. For carbene **4d** ca. 1 M cyclohexadiene had to be added to obtain the radical spectrum due to the much shorter lifetime of this carbene compared to the others. Within the resolution of the transient absorption spectra, all of the carbenes **4** and their corresponding radicals exhibited the same transient absorption maxima at 330 and 350 nm, respectively, which are red shifted with respect to diphenylcarbene and the diphenylmethyl radical. However, these wavelengths may not represent the true absorption maxima of the transient species because bleaching of the precursor diazo compounds occurs in this wavelength region also.

The lifetimes of the carbenes in hexane in the absence of quenchers were difficult to determine accurately due to the overlapping absorptions of the transient species produced; however, the lifetimes did appear to decrease as a function of ring size from ca. 10 μs in hexane for **4a** to ca. 500 ns in hexane for **4d**. This same trend is followed by the rate constants for isoprene quenching, and to a greater extent by the rate constants for alcohol quenching (vide infra).

The insertion reaction of carbenes with alcohols to form ethers is usually considered to occur from the singlet states of these species.[3] However, time-resolved experiments have shown that the ground triplet state of diphenylcarbene is efficiently quenched by methanol.[4,5] This has been explained by means of a mechanism in which the triplet state of diphenylcarbene is in thermal equilibrium with the singlet state (eq 5). According to this mechanism the rate at which the triplet state is quenched by methanol

$$^3\mathrm{DPC} \underset{k_{st}}{\overset{k_{ts}}{\rightleftharpoons}} {}^1\mathrm{DPC} + \mathrm{MeOH} \xrightarrow{k_s} \text{ether} \qquad (5)$$

(k_{st}(app)) is given by eq 6.[4,5] The value of k_s has been determined to be 5×10^9 M^{-1} s^{-1}.[5] Thus the ratio k_{ts}/k_{st}, and hence the free energy difference between the two spin states, can be determined from a knowledge of both k^t(app) and k_s. If the carbenes **4**, being

$$k^t(\text{app}) = k_s(k_{ts}/k_{st}) \qquad (6)$$

analogues of diphenylcarbene, react with alcohols according to the same mechanism, then the rate of quenching of the triplet states of these species by alcohols should be sensitive to the value of k_{ts}/k_{st}, which is of course related to the energy difference between the ground triplet and singlet states. The reaction of alcohols with the carbenes **4** was thus chosen to investigate the influence of the structures of these ground-state triplet carbenes on the efficiency of a "singlet-state" reaction.

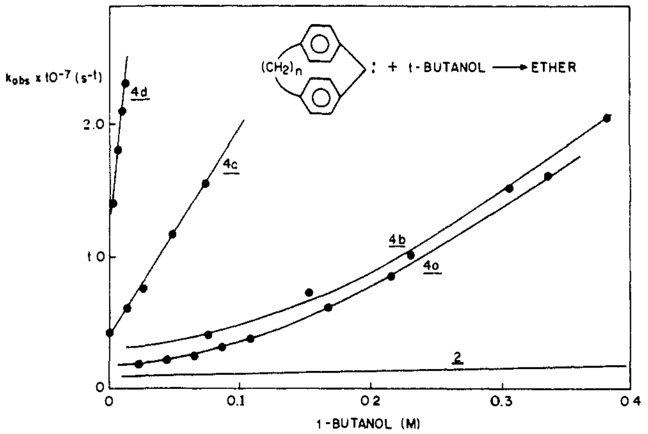


Figure 2. Plots of the rate of decay of the carbenes **2** and **4** in THF as a function of added *tert*-butyl alcohol.

Upon addition of methanol or *tert*-butyl alcohol to solutions of the diazo compounds **3a** and **3b** in hydrocarbon solvents, the rates of decay of the carbenes **4a** and **4b** (k_{obsd}) increased. However, plots of k_{obsd} vs. alcohol concentration were nonlinear.[10] In tetrahydrofuran solvent more linear plots were obtained with *tert*-butyl alcohol as the quencher and are shown in Figure 2 for each carbene. Very similar plots were obtained for each carbene with methanol. It is clear that the reactivity of each of the carbenes **4** toward these alcohols is greater than that of DPC and that the reactivity increases as the size of the methylene chain decreases. For the carbenes **4a** and **4b** the plots are still slightly curved at low quencher concentrations. This curvature is very reminiscent of the results obtained with picosecond techniques for quenching of singlet diphenylcarbene by methanol.[11] In that case the nonlinearity was attributed to solvent polarity effects upon the delicate carbene singlet/triplet equilibrium.

From the slopes of the plots of Figure 2 we can determine the rate constants for carbene quenching (k_q) shown in Table I. For the carbenes **4a** and **4b** the slopes of the plots of k_{obsd} between 0.15 and 0.4 M alcohol were taken as indicative of the quenching efficiency (see Figure 2). If we assume that the reaction of the carbenes **4** with alcohols can be described according to the same scheme as that for diphenylcarbene (eq 5 and 6), then the rate of quenching, k_q, is related to k_s and k_{ts}/k_{st}. Consequently, the increase in reactivity which is observed as a function of decreasing ring size in the carbenes **4** must be due to either an increase in k_s or an increase in k_{ts}/k_{st}. A higher value of k_s cannot account for the 350-fold increase in reactivity of **4d** with *tert*-butyl alcohol compared to DPC, since k_s for the latter carbene is only ca. 10 times smaller than the diffusion limit.[5] A more likely explanation is that k_{ts}/k_{st} increases due to a smaller free energy difference between the ground triplet states of these carbenes and their singlet states as a function of decreasing size of the methylene chain. Caution must be applied before equating the quenching constants k_q to the k^t(app) of eq 6, because of the possible solvent polarity effects observed for **4a** and **4b** and because of the possible inapplicability of the steady-state approximation for the singlet carbene as k_{ts}/k_{st} approaches unity. Assuming that the quenching of the

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[10] (a) Previously nonlinear plots of decay rate vs. alcohol concentrations have been observed in the reactions of phenylchlorocarbene (ref 10b). However, the present effects are not consistent with those observations since in this case similar behavior is found for methanol and *tert*-butyl alcohol, whereas for phenylchlorocarbene opposite curvature was observed for these two alcohols. (b) Griller, D.; Liu, M. T. H.; Scainao, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

[11] Sitzmann, E. V.; Langan, J. G.; Eisenthal, K. B. *Chem. Phys. Lett.* **1984**, *112*, 111.

[12] Lapin, S. C.; Brauer, B.-E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092.

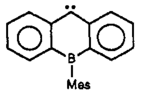
carbenes can be described according to eq 5, and that k_s for each carbene is the same as that for singlet diphenylcarbene, then values of k_{ts}/k_{st} of 0.04, 0.05, 0.14, and 0.4 can be estimated for carbenes, **4a**, **4b**, **4c**, and **4d**, respectively. At room temperature these are equivalent to free energy differences between the ground triplet and singlet states of 2.0, 1.8, 1.2, and 0.5 kcal M^{-1}, respectively. It should be emphasized that these values are only estimates, in view of the approximations and assumptions involved, and are only meant to serve as an indication of the effect of the change in structure within the series of carbenes **4**. The main conclusion to be drawn from these results is that the trend on going from carbene **4a** to carbene **4d** is to lower the energy of the singlet state with respect to the triplet state.

Recently it was suggested that eq 5 and 6 may not represent a valid mechanism for the reaction of diphenylcarbene with methanol.[13] Instead it was suggested that the triplet state of DPC reacts directly with the alcohol, via a surface crossing, to give the insertion product. This mechanism also predicts that the reaction rate should get faster for smaller values of ΔE_{ts} since the surface crossing should occur earlier along the reaction coordinate. Thus the conclusion that ΔE_{ts} decreases with decreasing ring size is consistent with either mechanism.[14]

Consistent with the proposal that the increased reactivity is due to a decrease in the triplet/singlet energy gap is the observation that the rate of quenching of the carbenes with 1,4-cyclohexadiene increases by only a factor of 7 from DPC to **4d**. For each carbene, upon addition of this quencher increased transient absorption signals attributable to radicals were observed, which implies that the same (hydrogen abstraction) reaction occurs in each case. This suggests that the overall reactivity of the triplet state, or the carbene as a whole, is not significantly raised but that it is the relative energy of the singlet and triplet states which is most influenced. The increased rate of quenching of the carbenes by isoprene (ca. 30 times faster for 4d compared to DPC) may reflect some participation of the singlet state, in addition to the triplet state, for those carbenes with sufficiently small energy gaps.

Of significant interest is the value of k_q of 2×10^9 M^{-1} s^{-1} for the reaction of **4d** with methanol. This is close to the directly determined rate constant of 5×10^9 M^{-1} s^{-1} for the reaction of singlet diphenylcarbene with methanol.[11] Thus carbene **4d** exhibits the highly interesting properties of reactions with oxygen and hydrogen donors at rates similar to other related ground-state triplet carbenes but reaction with methanol at a rate similar to a singlet carbene. This carbene appears to possess the properties of both triplet and singlet states! In this case it is probably not meaningful to talk about a ground state, since the lowest energy spin state probably depends upon the solvent, or other reaction conditions. The equilibrium between the two spin states is obviously efficient, and k_{ts}/k_{st} is probably close to unity.

Thus the data appear to provide clear experimental support for the predicted relationship between ΔE_{ts} and α and θ. The results are also consistent with the limited literature data on related systems. Schuster has rationalized the increased stability of the triplet state of carbene **5** relative to carbene **6** in terms of the increased bond angle at the carbene center in **5** compared to **6**, although the electronic effect of the boron atom has to be taken into account in this case.[12]



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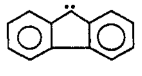

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Conclusion

The unique properties of the cyclophane carbenes **4** allow a study of the effect of conformation on the triplet/singlet splitting in diarylcarbenes, without drastically influencing the aryl molecular orbitals with other substituents. The results are clearly consistent with proposals that the triplet/singlet energy gaps in diarylcarbenes can be influenced by the hybridization at the carbenic center and the twist of the aryl rings.

Acknowledgment. The authors thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research.

Registry No. 1, 883-40-9; **2**, 3129-17-7; **3a**, 90279-04-2; **3b**, 90279-05-3; **3c**, 90296-74-5; **3d**, 90279-06-4; **4a**, 90279-08-6; **4b**, 90279-09-7; **4c**, 90279-10-0; **4d**, 90279-11-1; $H_2C{=}CHC(CH_3){=}CH_2$, 78-79-5; $(H_3C)_3COH$, 75-65-0; CH_3OH, 67-56-1; 1,4-cyclohexadiene, 628-41-1.

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

(14) The authors would like to thank a referee for this suggestion.