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THE TRIPLET GROUND STATE OF DI-TERT-BUTYLCARBENE

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Summary: STO-3G calculations indicate that the triplet state of di-*tert*-butylcarbene is on the order of 25 kcal/mol more stable than the singlet. Because of steric repulsions between the *tert*-butyl groups, the central CCC angles are 132.5° and 142° for the singlet and triplet, respectively. The normal alkyl group stabilization of the singlet is overridden by destabilization due to the sterically forced increase of the central angle.

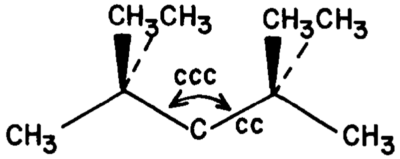
The parent carbene, methylene, has a triplet ground-state which is 9-11 kcal/mol lower in energy than the singlet.[1] Numerous experimental and theoretical studies show that the substitution of π-donors such as alkyl groups on methylene causes the lowest singlet state to be stabilized more than the triplet, and eventually the singlet becomes the ground state.[2] Quantitatively, this has been expressed by the relationship,[2a]

$$E(S) - E(T) \simeq 84.5\,\sigma^{o}_{R} + 13$$

where $\sigma_R{}^o$ is the empirical resonance substituent constant. Using this equation, with Exner's value for $\sigma_R{}^o$ of -0.08 for *tert*-butyl,[3a] di-*tert*-butylcarbene is predicted to have the triplet state 0.5 kcal/mol lower in energy than the singlet. With the much larger value of $\sigma_R{}^o$ of -0.17,derived from Taft's compilation,[3b] the singlet is predicted to be 16 kcal/mol more stable than the triplet. Recently, Gano *et al.* have studied di-*tert*-butylcarbene in a matrix at low temperature.[4] The triplet carbene was observed by esr, and the ratio of zero-field parameters led to a rough estimate of the central CCC bond angle of 143°.[4]

We have carried out *ab initio* calculations on di-*tert*-butylcarbene which indicate that the triplet state is considerably more stable than the singlet state due to the steric repulsion between the *tert*-butyl groups, which opens the singlet carbene CCC angle dramatically. The theoretically predicted CCC bond angle is found to be essentially identical to that estimated experimentally.

Calculations were performed using GAUSSIAN 80[5] and the STO-3G minimal basis set with optimization of the central CCC bond angle and central CC bond lengths. The carbenes were assumed to have C_{2v} symmetry, all-staggered conformations, and both tert-butyl groups were fixed at standard bond lengths and angles.[6,7] Final geometries and energies are shown below.



singlet: ccc = 132.5°; cc = 1.5733 Å ; E = -346.99732 a.u.

triplet : ccc = 142.4° ; cc = 1.5361 Å ; E = -347.08006 a.u.

The calculated CCC angle of the triplet is 142°, in remarkable agreement with the Gano et al. experimental estimate.[4] The singlet state equilibrium bond angle is 132.5°. Since the triplet carbene is calculated by UHF techniques, the stability of this species is greatly overemphasized relative to the stability of the singlet, for which the computation is performed by an RHF calculation. Although the error in the singlet-triplet gap is not a constant for different carbenes, we can estimate the true gap for di-tert-butylcarbene by assuming that the STO-3G calculated singlet-triplet gap (51.9 kcal/mol) is roughly in error by the amount (27.3 kcal/mol) by which the methylene ST gap is overemphasized at the same theoretical level;[2a] with this assumption the di-tert-butylcarbene singlet-triplet gap is predicted to be on the order of 25 kcal/mol, with the triplet state more stable. This surprisingly large singlet-triplet gap is the result of the forced increase in bond angles in the singlet and, to a lesser extent, the triplet, due to the bulk of the tert-butyl groups. In methylene, the calculated CCC bond angles in the singlet and triplet are 100.4° and 125.5°, respectively, at the theoretical level used here for di-tert-butylcarbene. For dimethylcarbene, the calculated angles are 107.6° and 127.2°. Thus, the CCC angles are increased by 25° in the singlet and 15° in the triplet states of di-tert-butylcarbene, as compared to the values in dimethylcarbene, whereas the geometries of both dimethylcarbene states are only slightly perturbed by steric repulsions from the values in methylene itself. The 32° increase in the central bond angle of singlet di-tert-butylcarbene over that of methylene is 1.7 times larger than the experimental increase in the central angle of di-tert-butylmethane[8] as compared to methane (19°).

In order to insure that our rigid tert-butyl assumption does not introduce artificial errors into the calculations, partial optimizations of mono-tert-butylcarbene were also performed with the same assumptions as for the di-tert-butyl species. The CC angles are calculated to be 102.9° and 126.0° for the singlet and triplet, respectively, only 2.5° and 0.5° larger than those predicted for CH_2 at the same computational level. The estimated S-T gap of 7.6 kcal/mol (triplet more stable), from subtraction of 27.3 kcal/mol from the computed gap, is nearly the same as that (6.2 kcal/mol) predicted from the $\sigma_R{}^o$ relationship, and Exner's $\sigma_R{}^o$ value.

Finally, in order to determine the effect of increasing bond angles on S-T gaps, we performed STO-3G calculations on methylene, dimethylcarbene, and tert-butyl carbene with the HCH or CCC bond angles fixed at the CCC angle obtained for di-tert-butylcarbene. The STO-3G calculated singlet-triplet energy gaps of the three carbenes increased by 16, 14, and 15 kcal/mol as compared to those obtained from optimized geometries. Calculations by Schaefer et al.,[9] using a much larger basis set, also show that $^1A_1$ singlet methylene has a steeper energy gradient with respect to bond angle distortions than $^3B_1$ triplet methylene.

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(7) The rotational arrangement of the *tert*-butyl groups is not critical to these arguments. At the optimized geometries, rigid rotation of one *tert*-butyl group by 60° causes 0.6 and 0.1 kcal/mol increases in energy for the singlet and triplet, respectively. Rotation of both groups by 60° causes 15.0 and 0.4 kcal/mol energy increases, respectively. The fully optimized structure may have the *tert*-butyl groups slightly rotated away from the ideal staggered arrangement, as found for di-*tert*-butylmethane.[8]

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