J. Am. Chem. Soc. **2001,** *123,* 4331−4335

The Almost Bottleable Triplet Carbene: 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene

H. Lee Woodcock, Damian Moran, Paul von Ragué Schleyer, and Henry F. Schaefer, III*

Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602.

Received September 29, 2000. Revised Manuscript Received February 23, 2001

Abstract: Computations on 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (**1**) using *ab initio* and density functional theory methods underscore the unusual stability of the triplet over the singlet state. At the B3LYP/6-311G(d,p) level, the triplet state had a slightly bent central C−C−C bond angle of 167°, whereas this angle in the singlet was 134°. The B3LYP singlet−triplet splitting (12.2 kcal/mol) was larger than that of the parent molecule (5.8 kcal/mol), diphenylcarbene (**2**), which also has a triplet ground state. The energy of a suitable isodesmic reaction showed the triplet and singlet states of **1** to be *destabilized*, by 6.3 and 12.5 kcal/mol, respectively, due to the combined effects of the CF_3, Br, and alkyl substituents. The linear-coplanar form of ^{3}**1**, which might facilitate dimerization or electrophilic attack at the more exposed diradical center, was prohibitively (35.9 kcal/mol) higher in energy. Our results confirm Tomioka's conclusion that the triplet diarylcarbene, ortho-substituted with bulky CF_3 and Br substituents, is persistent due to steric protection of the diradical center. Dimerization and other possible reaction pathways are inhibited, not only by the bulky ortho substituents but also by the para alkyl groups. The increase in stability of the triplet (^{3}**1**) state relative to the singlet (^{1}**1**) state does not influence the reactivity directly.

Introduction

Stable carbenes provide insights into transient organic species.[1−4] Singlet carbenes, persistent at room temperature, are well known: the recent examples reported by Igau et al.,[5] Arduengo et al.,[6] and Buron et al.[3] benefit particularly from stabilizing electronic effects.

In contrast, the steric (kinetic stabilization) effects of bulky substituents are considered to be more important for the persistence of triplet carbenes.[7−12] Besides preventing access to the diradical center, such groups tend to increase the central angle and hence are said to "stabilize the carbene thermodynamically, since the wider the angle the more stable the triplet state becomes with respect to the singlet".[12] The trifluoromethyl group was found to be an ideal protector of triplets due to its steric bulk and lack of reactivity toward carbenic centers.[8,9] Culminating a series of impressive investigations, Hirai and Tomioka[7−10,12] demonstrated that triplet 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (Figure 1) has a half-life of ∼16 min at 20 °C and an indefinite shelf life at −40 °C. In related work, para alkyl substituents were found to increase triplet persistence.[7]

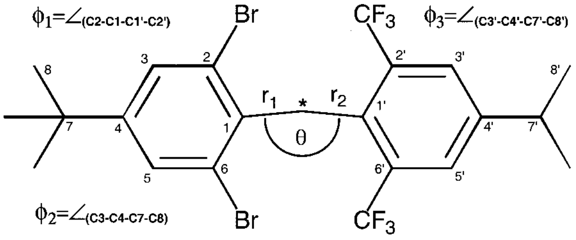

Figure 1. Geometric parameters r_1, r_2, θ, and ϕ measured from the optimized geometries of 2,6-dibromo-4-tertbutyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (**1**). Hydrogens omitted for clarity.

In light of the results of Tomioka et al.[7−10,12] and of the potential for triplet carbenes to be used as organic ferromagnets,[13,14] we have investigated the complete experimental system **1**, not only with its bulky ortho CF_3 and Br groups but also with the para alkyl substituents. We computed the geometries of the singlet (^{1}**1**) and the triplet (^{3}**1**) states, the singlet−triplet splitting, and the energetic effects of the substituents on both ^{1}**1** and ^{3}**1** in an effort to ascertain reasons for the unusual persistence of the triplet. The parent diphenylcarbene system **2** was also studied for comparison, and a suitable isodesmic reaction was used to ascertain the energetic effects of the substituents in ^{1}**1** and ^{3}**1**.

We also computed the approximate barrier to linearity of ^{3}**1** and examined a highly congested triplet coplanar structure to give an approximation of the energetic penalty required to gain access to the diradical center.

---

(1) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913.

(2) Bourissou, B.; Guerret, O.; Gabbai, F. P.; G., B. *Chem. Rev.* **2000**, *100*, 39.

(3) Buron, C.; Gornitzke, H.; Romanenko, V.; Bertrand, G. *Science* **2000**, *288*, 834.

(4) Herrmann, W. A.; Kocher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(5) Igau, A.; Grutzmacher, H.; Baceirdo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463.

(6) Arduengo, A. J.; Harlow, R. L.; Kline, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(7) Hu, Y.; Hiari, K.; Tomioka, H. *J. Phys. Chem.* **1999**, *103*, 9280.

(8) Hiari, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213.

(9) Tomioka, H.; Taketsuji, K. *J. Chem. Soc., Chem. Commun.* **1997**, 1745.

(10) Tomioka, H.; Hattori, M.; Hiari, K.; Murata, S. *J. Am. Chem. Soc.* **1996**, *118*, 8723.

(11) Harrison, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 4112.

(12) Itakura, H.; Mizuno, H.; Hirai, K.; Tomioka, H. *J. Org. Chem.* **2000**, *65*, 8797.

(13) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(14) Iwamura, H. *Adv. Phy. Org. Chem.* **1990**, *26*, 179.

10.1021/ja003552q CCC: $20.00

Table 1. Absolute Energies (in hartrees) and Singlet−Triplet Energy Separations (S−T) (in kcal/mol) for Singlet and Triplet 2,6-Dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (**1**), Diphenylcarbene (**2**), and Methylene (CH_2)[a]

molecule	program	method	singlet	triplet	S−T
1	Q-Chem	B3LYP	−6596.981 12[b]	−6597.000 72[b]	12.3
1	Q-Chem	BLYP	−6597.594 78[b]	−6597.607 96[b]	8.3
1	Q-Chem	HF	−6586.369 47	−6586.452 70	52.2
1	G98	B3LYP	−6598.025 47[b]	−6598.044 53[b]	12.0
1	G98	BLYP	−6597.593 91[b]	−6597.607 23[b]	8.4
1	G98	HF	−6586.369 47	−6586.452 70	52.2
2	G98	B3LYP	−501.415 07[c]	−501.424 28[c]	5.8
CH_2	G94	B3LYP	−39.144 35[d]	−39.164 47[d]	12.6
CH_2	G98	BLYP	−39.123 41	−39.140 83	10.9

[a] Energies refer to structures optimized with the 6-311G(d,p) basis set at each level of theory. [b] Refer to refs 28 and 29 to account for energy difference between Q-Chem and G98 DFT calculations. [c] Refer to Table 2 for more diphenylcarbene results. [d] Results for methylene were obtained from ref 31.

Table 2. HF/SCF and DFT Optimized Geometric Parameters for Singlet (^{1}**1**) and Triplet (^{3}**1**) 2,6-Dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene[a]

state	method	r_1 (Å)[b]	r_2 (Å)[b]	θ^o,[b]	ϕ_1^o,[b]	ϕ_2^o,[b]	ϕ_3^o,[b]
singlet (^{1}**1**)	B3LYP	1.393	1.403	134.2	79.1	177.3	119.6
	BLYP	1.387	1.394	138.7	80.7	173.5	112.8
	HF	1.432	1.452	126.7	80.1	179.8	118.1
triplet (^{3}**1**)	B3LYP	1.368	1.368	176.3	90.7	178.2	110.0
	BLYP	1.368	1.369	175.8	84.2	171.4	122.8
	HF	1.389	1.382	158.9	94.6	180.0	117.1

[a] All structures were optimized, using Q-Chem, in C_1 symmetry with the 6-311G(d,p) basis set at each level of theory (r_1 is the C−C distance to the Br substituted ring, r_2 is the C−C distance to the CF_3-substituted ring). [b] See Figure 1 for details of bond lengths (r), angles (θ), and dihedrals (ϕ).

Methods

Quantum chemical computations were performed using the Gaussian 98[15] and Q-Chem[16] RHF (singlet), UHF (triplet), and DFT algorithms. Spin-unrestricted Kohn−Sham orbitals[17] were used for the DFT computations. We converged Cartesian gradients to at least 1×10^{-4} hartree/bohr in Gaussian 98 and in Q-Chem. Numerical integration of the functionals used a pruned grid consisting of 75 radial shells with 302 angular points per shell, the so-called (75,302)p in Gaussian 98,[15] and the standard quadrature grid (SG-1),[18] consisting of 50 radial shells with 194 angular points per shell, in Q-Chem. The Q-Chem SG-1 grid has been shown to give numerical integration errors on the order of 0.2 kcal/mol for medium-sized molecules.[19]

Geometries for both the singlet and triplet states were optimized via standard analytic derivative methods.[20−22] At the pure DFT level, the 1988 exchange functional of Becke (B)[23] was employed in conjunction with the Lee, Yang, and Parr (LYP)[24] correlation functional (BLYP). Another of Becke's exchange functionals (B3)[25] was used at the hybrid HF/DFT level, also in conjunction with the standard LYP correlation functional (B3LYP). All computations used the Pople triple-ζ split valence set, 6-311G(d,p).[26] Determination of geometrical parameters and energies for ^{1}**1** and ^{3}**1** was done using Q-Chem.[16] Optimizations as well as energetic and force constant determinations of ^{1}**2**, ^{3}**2**, and the reference compounds needed to evaluate the isodesmic equation were carried out with Gaussian 98.[15] Note that the VWN[27] correlation functional is implemented differently in Q-Chem and in Gaussian 98, and the absolute energies given by the two programs differ.[28,29]

Results

The triplet (^{3}**1**) and singlet (^{1}**1**) total energies and singlet−triplet splittings (S−T) are summarized in Table 1. The triplet states were lower in energy at all levels of theory. Density functional theory (DFT) methods, which recover some dynamic correlation energy, have been shown to be a cost-effective way of estimating singlet−triplet energy separations.[30] In contrast, HF/SCF theory is well known to perform poorly due to overestimation of the relative stability of the triplet state;[26,30] this is shown here by the greater than 40 kcal/mol deviation between the HF/SCF and B3LYP S−T splitting results. The S−T differences for ^{1}**1** and ^{3}**1** computed using B3LYP came out to be nearly the same as those for CH_2 at the same level of theory.[26,30−47]

---

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian Version A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(16) White, C. A.; Kong, J.; Maurice, D. R.; Adams, T. R.; Challacombe, M.; Schwegler, E.; Dombroski, J. P.; Ochsenfeld, C.; Oumi, M.; Furlani, T. R.; Adamson, R. D.; Nair, N.; Lee, A. M.; Ishikawa, N.; Graham, R. L.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M. Q-Chem Version 1.2, Q.-Chem Inc., Pittsburgh, PA, 1998. Q-Chem 2.0. *J. Comput. Chem.* **2000**, *21*, 1532.

(17) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(18) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett* **1993**, *209*, 506.

(19) Dombroski, J. P. In Q-Chem, Inc.: Export PA, 1998.

(20) Pulay, P. *Mol. Phys.* **1969**, *17*, 197.

(21) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4, pp 153−185.

(22) Yamaguchi, Y.; Osamura, Y.; Goddard, J. D.; Schaefer, H. F. *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory*; Oxford University Press: New York, 1994.

(23) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(27) Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(28) Vosko, Wilk, and Nusair actually recommended implementation of the VWN5 functional. Gaussian Inc. implemented VWN3 as a part of the B3LYP functional, and Q-Chem Inc. implemented VWN5. This leads to a substantial energy difference between G98 and Q-Chem computations using the hybrid B3LYP functional.

(29) Roland, H. H.; Koch, W. *Chem. Phys. Lett.* **1997**, 268, 345.

(30) Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., Schreiner, P. R., Eds.; John Wiley & Sons. 1998; pp 183−196.

(31) Dehareng, D.; Dive, G. *J. Comput. Chem.* **2000**, *21*, 483.

(32) Das, D.; Whittenburg, S. L. *J. Mol. Struc (THEOCHEM)* **1999**, *492*, 175.

(33) Bender, C. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 4984.

(34) Bernheim, R. A.; Bernard, H. W.; Wang, P. S.; Wood, D.; Skell, P. S. *J. Chem. Phys.* **1970**, *53*, 1280.

(35) Bunker, P. R.; Jensen, P. *J. Chem. Phys.* **1983**, *79*, 1224.

(36) Engelking, P. C.; Corderman, R. R.; Wendolowski, J. J.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C. *J. Chem. Phys.* **1981**, *74*, 5460.

(37) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 305.

(38) Hayden, C. C.; Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T. *J. Chem. Phys.* **1982**, *76*, 3607.

(39) Herzberg, G.; Shoosmith, S. *Nature* **1959**, *183*, 1801.

(40) Herzberg, G. *Proc. R. Soc.* **1961**, *A262*, 291.

(41) Herzberg, G.; Johns, J. W. C. *J. Chem. Phys.* **1971**, *54*, 2276.

(42) Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1988**, *89*, 1327.

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

(44) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251.

(45) McLaughlin, D. R.; Bender, C. F.; Schaefer, H. F. *Theor. Chim. Acta* **1972**, *25*, 352.

(46) Sears, T. J.; Bunker, P. R. *J. Chem. Phys.* **1983**, *79*, 5265.

(47) Wassermann, E.; Yager, W. A.; Kuck, V. J. *Chem. Phys. Lett.* **1970**, *7*, 409.

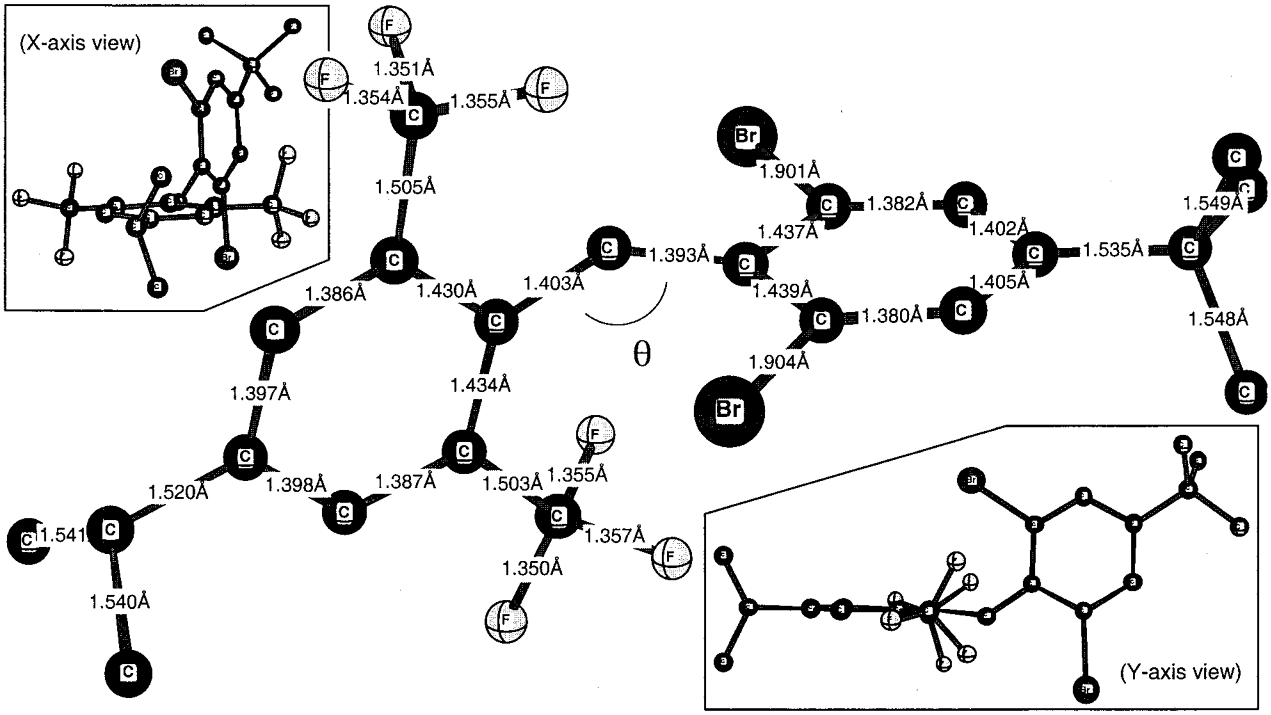

Figure 2. Q-Chem B3LYP optimized geometry of singlet 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (^{1}**1**). The central C−C−C optimized bond angle (*θ*) is 134.2°. Hydrogens omitted for clarity.

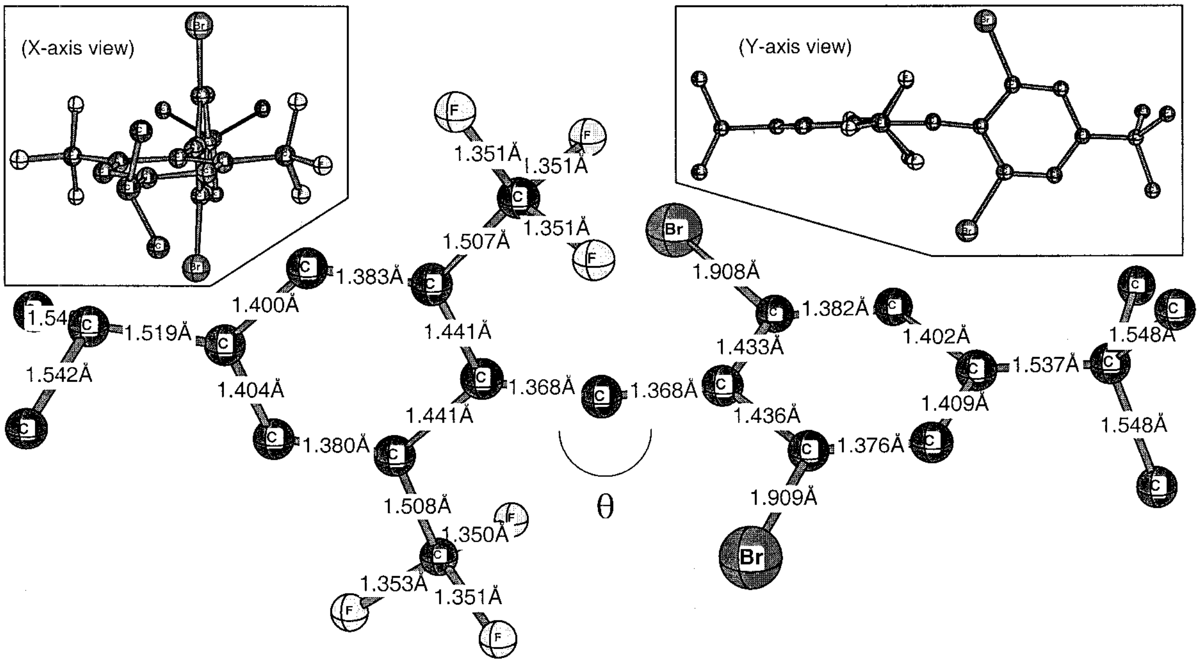

Figure 3. Q-Chem B3LYP optimized geometry of triplet 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (^{3}**1**). The central C−C−C optimized bond angle (*θ*) is 176.3°. Hydrogens omitted for clarity.

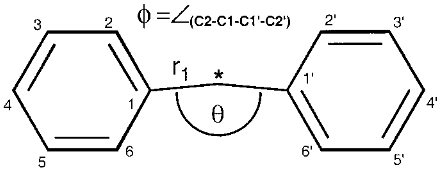

Figure 4. Diphenylcarbene (**2**) geometric parameters r_1, *θ*, and *ϕ*. Hydrogens omitted for clarity.

At all levels of theory, the alkyl groups (isopropyl, *tert*-butyl) adopted comparable conformations relative to the rings to which they were bonded. The isopropyl dihedral angles, ϕ_3 (Figure 1, Table 2), were approximately equal in ^{1}**1** and ^{3}**1**; similarly, the *tert*-butyl dihedral angles, ϕ_2 (Figure 1, Table 2), nearly were the same for the two states. The isopropyl hydrogen is oriented in the plane of the aromatic ring to which it is attached, while the *tert*-butyl group is most stable when a methyl carbon lies in the plane of the ring. Optimizations and vibrational frequency analyses of 1,5-dibromo-3-isopropylbenzene and of 1,5-di(trifluoromethyl)-3-*tert*-butylbenzene confirned these results. The torsional angle, ϕ_1 (Figure 1, Table 2), revealed a nearly perpendicular arrangement between the aromatic ring planes at all levels of theory.

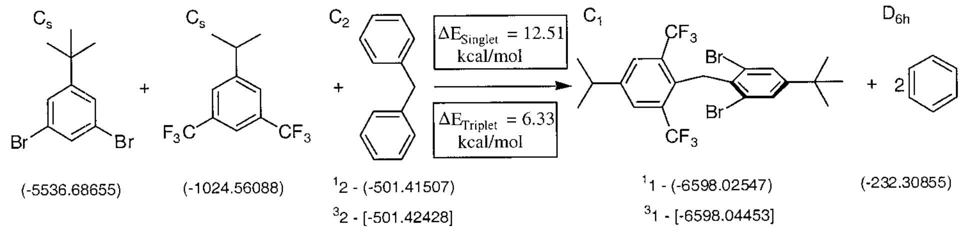

Figure 5. Isodesmic reaction scheme used to estimate the contribution of aryl ring substitution to the stability of ^{1}**1** and ^{3}**1**. Hydrogens omitted for clarity. G98 B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p) energies (kcal/mol) are shown below structures. Two energies (kcal/mol) are shown for singlet (in parentheses) and triplet (in brackets) spin states.

Table 3. Diphenylcarbene, Singlet and Triplet Absolute Energies (in hartrees), First Harmonic Vibrational Frequencies (or imaginary frequency), and Optimized Geometric Parameters (Figure 4)[a]

state	symm	energy	ω (cm^{-1})	r$_1$ (Å)	θ°	ϕ_1°
singlet	C_{2v}	−501.388 29	372*i*	1.436	119.7	0.0
	C_s	−501.407 17	169*i*	1.435, 1.441	118.8	75.0
	C_2	−501.415 07	57	1.431	119.5	59.1
triplet	D_{2h}	−501.415 10	120*i*	1.391	180.0	0.0
	D_{2d}	−501.421 79	36*i*	1.371	180.0	90.0
	D_2	−501.421 80	36*i*	1.371	180.0	90.0
	C_{2v}	−501.421 47	53*i*2	1.405	147.0	0.0
	C_2	−501.424 28	44	1.400	143.1	67.8

[a] All structures were optimized using G98 and the B3LYP/6-311G(d,p) level of theory. The singlet−triplet separation was 5.78 kcal/mol at the optimized C_2 geometries.

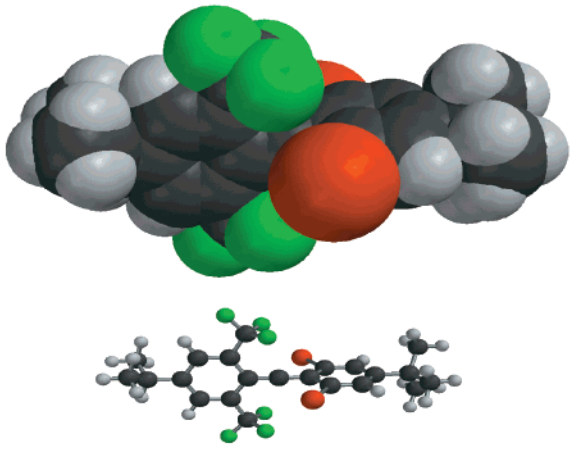

Figure 6. Space filling model of triplet 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (^{3}**1**), compared with a ball-and-stick model.

The flatness of the potential energy surface was shown by a number of computations in which the central C−C−C angle was varied. For example, a B3LYP structure with a 167.1° bond angle obtained by optimization using the default convergence criteria had an energy of only 0.19 kcal/mol greater than the lowest energy structure which had a bond angle of 176.3°. Note, that the geometries given in Table 2 are subject to cutoff limits in optimization algorithms; tighter limits were not employed due to the flat potential energy surface and large computational cost involved.

The C−C−C bond angle (θ) and C−C carbene−ring distances, designated r_1 and r_2, of 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (Figure 1) are summarized in Table 2; the B3LYP optimized singlet and triplet states are shown in detail in Figure 2 and Figure 3, respectively. From the singlet carbene C−C bond distances (r_1 is shorter than r_2, Figure 2), it is clear that some stabilization occurs via donation of electron density from the bromine-substituted aromatic ring into the vacant p orbital on the diradical center. Conversely, in the triplet state (Figure 3), where carbene p orbitals are singly occupied and orthogonal, both aromatic rings interact equally with the diradical center. Because of the flat potential energy surfaces, the geometries vary among the different methods (Table 2). The major differences, between the HF and DFT geometries, are due to the lack of electron correlation and poor treatment of conjugation by HF theory.[26,30] The B3LYP and BLYP functionals describe p−π conjugation better and predict a larger C−C−C angle in comparison to HF theory.

Diphenylcarbene (Figure 4) singlet (^{1}**2**) and triplet (^{3}**2**) structures were optimized at the B3LYP level using Gaussian 98. Vibrational frequency analyses confirmed that both the singlet and the triplet minimums have C_2 equilibrium geometries (Table 3), in agreement with experimental deductions.[48] The central C−C bond length (r_1) was longer in ^{1}**2** than in ^{3}**2**, which is consistent with the trend in the optimized r_1 and r_2 bond lengths of ^{1}**1** and ^{3}**1**.

Bond distances, r_1 and r_2, were shorter in ^{1}**1** and ^{3}**1** than in ^{1}**2** and ^{3}**2**. The differences were computed to be 0.038 (Δr_1) and 0.028 Å (Δr_2) for the singlet and 0.032 Å for the triplet (where $r_1 = r_2$). The changes in the bond lengths were primarily due to the central C−C−C bond angles in **1** and **2**. These central angles (Tables 2 and 3) are bent significantly more in **2** than in **1**: ^{1}**2** (119.5°) versus ^{1}**1** (134.2°) and ^{3}**2** (143.1°) versus ^{3}**1** (176.3°). For example, when ^{3}**2** was optimized in D_2 symmetry (180°), the r_1 distance was decreased by 0.031 Å relative to that of ^{3}**2** optimized in C_2 symmetry. The triplet diphenylcarbene C−C−C bond angle ($\theta = 143.1°$) comports with the $\theta \sim 150°$ experimental estimate for triplet diphenylcarbene.[49]

The S−T energy separation for **2,** only 5.8 kcal/mol at B3LYP using G98, was significantly lower than the 12.0 kcal/mol computed for **1** and also agreed well with the 3−5 kcal/mol experimental estimate.[50]

A suitable isodesmic reaction (Figure 5) shows that both ^{1}**1** and ^{3}**1** are *destabilized* (by 12.5 and 6.3 kcal/mol, respectively) by the addition of the bulky substituents (at B3LYP). Tomioka's assertion that the substituents "stabilize the triplet thermodynamically" does not refer to the absolute stabilization (the triplet actually is destabilized) but to the increase in S−T separation. Also, widening the angle of ^{3}**1** from equilibrium has very little effect on its energy. This also is true for the parent diphenylcarbene triplet (Table 3), where the barrier to linearity is only 1.4 kcal/mol.

To underscore the steric protection of the carbenic center in ^{3}**1**, we evaluated the energetic penalty required to open the

---

(48) Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731.

(49) Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *J. Chem. Phys.* **1964**, *40*, 2408.

(50) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543. M. S. Platz, private communication.

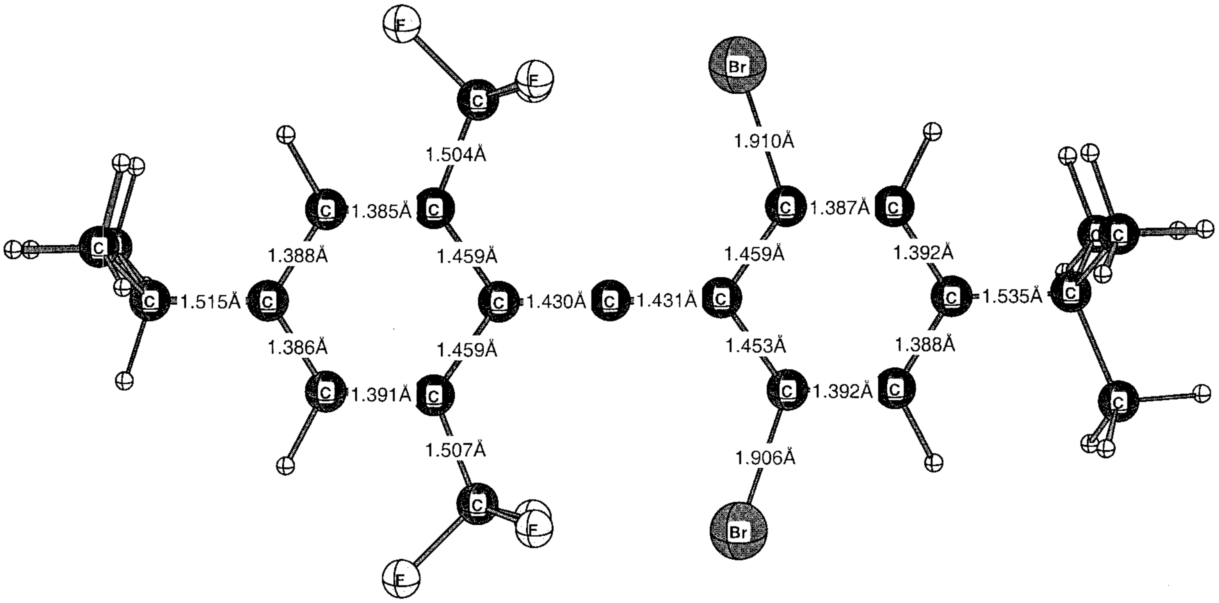

Figure 7. Q-Chem, B3LYP/6-311G(d,p), optimized triplet state of 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (^{3}**1**) in a highly congested (C_s) linear-coplanar conformation.

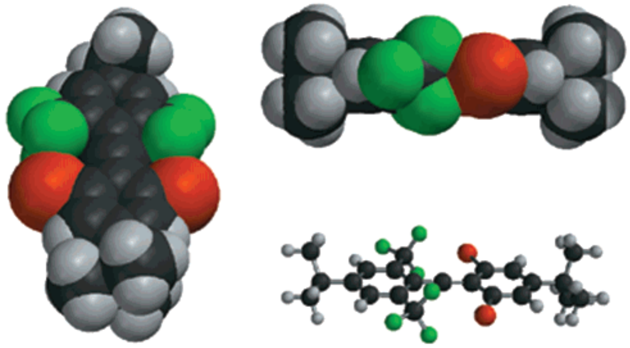

Figure 8. Space filling model of the highly congested linear-coplanar conformation of triplet 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene (^{3}**1**), optimized at B3LYP/6-311G(d,p).

central angle and make the diradical center more accessible. However, this opening would result in greater internal congestion. For example, in a nearly linear-coplanar configuration of the triplet state, the bulky CF_3 and Br substituents would collide in the plane of the two rings (Figures 6−8). This coplanar structure, optimized using Q-Chem's constrained algorithm at B3LYP/6-311G(d,p), resulted in an energy increase of 35.9 kcal/mol with respect to ^{3}**1**. Consequently, before this rather extreme coplanar structure is reached, the triplet state should cross to the singlet, since only 17.9 kcal/mol is needed for optimized ^{3}**1** to undergo interstate conversion to the singlet at the optimized ^{3}**1** geometry. Rotation around the C−C single bonds of the ^{3}**1** carbene carbon would also be inhibited. Consequently, the persistence of the triplet state results from the steric protection of the diradical.

Conclusions

We agree with Tomioka et al. that the triplet state of 2,6-dibromo-4-*tert*-butyl-2′,6′-bis(trifluoromethyl)-4′-isopropyldiphenylcarbene is more persistent due to the steric hindrance of the large CF_3 and Br substituents. However, our analysis of ^{3}**1** does not confirm Tomioka's implication that expansion of the central C−C−C bond angle contributes additional stability due to thermodynamic effects in the absolute sense. Larger S−T gaps have been stated to "stabilize" the triplet with respect to the singlet when bulky substituents are present.[7−12] In contrast, our data show that the substituents actually *destabilize* both ^{1}**1** and ^{3}**1**, with respect to diphenylcarbene, but do so more for ^{1}**1** than for ^{3}**1**. Although singlets are generally more prone to electronic stabilization effects, the isodesmic reaction for ^{1}**1** (Figure 5) is endothermic; even more so than the triplet. The reason seems clear—the intramolecular steric interactions are more adverse in the singlet, with its smaller internal bond angle, than in the triplet. The central C−C−C angle in the triplet diphenylcarbene is of minor importance energetically. The potential energy surfaces of the triplet states, ^{3}**1** and ^{3}**2**, are extremely flat and changes in the carbene angles have little effect on the energies. Only 1.4 kcal/mol is required to linearize triplet diphenylcarbene (^{3}**2**) from its 143° equilibrium geometry. The steric effects of the bulky substituents in ^{3}**1** resulting in a persistent carbene are due to the blocking of attack by external reagents rather than by internal effects (widening the bond angle).

The space filling model (Figure 6) shows just how effective the large substituents should be in protecting the carbenic center (as well as aryl rings) from reaction. The deformation energy required to expose the carbenic center to attack is prohibitively large. Hence, ^{3}**1** is persistent due to the steric protection, which precludes dimerization and other reactions, rather than to thermodynamic stabilization.

Acknowledgment. This research was supported by the U.S. National Science Foundation Grant: CHE-9815397 and by the University of Georgia. We thank Dr. Yukio Yamaguchi, Dr. Kai Exner, and Dr. Steve Wesolowski for helpful discussions.

JA003552Q