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Theoretical Study of Tetramethyl- and Tetra-*tert*-butyl-Substituted Cyclobutadiene and Tetrahedrane

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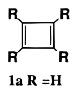
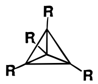
The tetramethyl and tetra-*tert*-butyl derivatives of cyclobutadiene and tetrahedrane have been studied with ab initio and density functional methods. The ring in tetra-*tert*-butylcyclobutadiene displays very unequal bond lengths (1.354, 1.608 Å) and confirms the earlier suspicion that the low-temperature X-ray structure was distorted. The C−C single bonds have the longest separations found to date between sp^2-hybridized carbons. Tetra-*tert*-butyltetrahedrane, which prefers T over T_d symmetry, is calculated to be 1.5 kcal/mol more stable than tetra-*tert*-butylcyclobutadiene (B3LYP/6-311+G(d)//B3LYP/6-31G(d)). The dications, $C_4R_4^{2+}$, dianions, $C_4R_4^{2-}$, and dilithiated species, $Li_2C_4R_4$ ($R = H$, Me, *t*-Bu), also were studied to determine the effect of substitution on structure and stability. Finally, NICS (nucleus-independent chemical shifts) values were calculated and showed, as expected, the dications and dianions ($4n + 2$ π-electrons) to be aromatic (negative NICS(0)) and the cyclobutadienes to be antiaromatic (positive NICS(0)).

Introduction

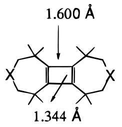
The exciting history of cyclobutadiene (**1**) and of tetrahedrane (**2**) has been punctuated with commas,[1] periods,[2] and question marks.[3] According to theoretical expectations, singlet cyclobutadiene (**1a)** should have a planar rectangular equilibrium structure with D_{2h} symmetry; the square structure (D_{4h}) represents the transition state joining two equivalent minima on the singlet potential energy surface.[1−3] Triplet cyclobutadiene (^{3}**1a)** is predicted to have a square minimum which is about 6−10[4,5] kcal/mol above the rectangular singlet and 4−7[4,5] kcal/mol above the singlet square transition state.



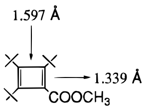
1a R =H
1b R=Me
1c R=t-Bu



2a R =H
2b R=Me
2c R=t-Bu



3a X = S
3b X = CH$_2$



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The structure of the parent cyclobutadiene **1a** has not been determined due to its high reactivity. It has been observed at low temperature in inert matrices[1] and immobilized more recently at room temperarure in hemicarcerand.[6] However, many structures have been reported for substitituted cyclobutadienes. For example, X-ray analyses have been reported for the stable cyclobutadiene derivatives **3**[7] and **4**,[8] which showed pronounced bond alternations. The double bonds, 1.344 and 1.339 Å, are normal in length but the 1.600 and 1.597 Å single bond lengths are much longer than usual.

It was therefore very surprising that the first X-ray analysis of **1c**[9] at room temperature showed only slight alternations in the ring carbon distances (1.464 and 1.482 Å). The quaternary C atoms of the *tert*-butyl groups deviated from the ring plane by 0.37 Å above or below in an alternating fashion. The four-membered ring itself was not planar but was folded with a dihedral angle of 170°. The nearly equal ring CC lengths were explained on the basis of steric interactions which were said to elongate the double bonds in **1c**. The short H···H distances of 1.84 Å also resulted in torsional angles of about 28° between the *tert*-butyl groups.

The publication of the X-ray determination of **1c** led Borden et al.[10] to perform quantum mechanical model calculations on **1a**, and to conclude that the almost square cyclobutadiene skeleton in the crystal is a plausible equilibrium structure for **1c**, since they thought the bulky *tert*-butyl groups might exert a considerable “quadratization effect”. They found that the large increase in the lengths of the double bonds in cyclobutadiene causes a relatively small energy increase. The energy increases are minimized if, concomitant with double-bond lengthening, single-bond shortening occurs.

However, Ermer and Heilbronner[11] supported a more rectangular structure for tetra-*tert*-butylcyclobutadiene (**1c)** by three different lines of reasoning.

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1. The photoelectron spectra of **1c** and **4**[7] are so similar (particularly those of **1c** and **3b**) that the four-membered ring structures should be closely related.[12]

2. Empirical force field calculations[13] indicated that the apparent elongation of the double bond of 0.12 Å (1.46−1.34 Å, **1c**−**3**,**4**) for rectangular **1c** reduces strain energy by only 0.4 kcal/mol.

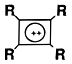
3. The observed structure of **1c** at room temperature may well be a consequence of a dynamic or static disorder in the crystal.

Because of this discrepancy concerning the near equal bond distances in **1c**, Irngartinger reinvestigated[11] the X-ray structure at −30 and −150 °C. The CC lengths at −30 °C (1.466 and 1.492 Å) do not differ significantly from the room temperature data.[9] However, measurements at −150 °C showed noticeably larger bond alternation (1.441 and 1.526 Å). The "temperature dependence" of the structure was explained by static or dynamic disorder in the crystal at room temperature. Indeed, a detailed later analysis of the anisotropic displacement parameters U_{ij} of the carbon atoms in the −150 °C structure concluded that residual disorder is still present at this temperature.[15] The corrected results are compatible with an averaged superposition of two rings with sides approximately 1.60 and 1.34 Å but situated with different orientations in the crystal. These bond lengths agree with values found in the other twisted cyclobutadiene derivatives (**3** and **4**).[7,8]

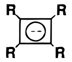
Tetra-*tert*-butyltetrahedrane (**2c**) can be formed from tetra-*tert*-butylcyclobutadiene (**1c**) by photolysis,[2] while the reverse reaction takes place thermally with an activation barrier of 26 kcal/mol.[2d] An ab initio study of the interconversion in the parent C_4H_4 system predicts an activation energy of about 30 kcal/mol.[16a]

Cyclobutadiene Dication and Dianions

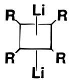
In contrast to neutral cyclobutadiene (**1**), its dication (**5**) and dianion (**6**) should be aromatic according to the Hückel rule.



5a R =H
5b R=Me
5c R=t-Bu



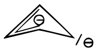
6a R =H
6b R=Me
6c R=t-Bu



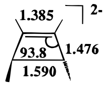
7a R =H
7b R=Me
7c R=t-Bu

Extensive calculations, however, indicate that species **5a**[17] is aromatic but **6a**[17e,f,18] is non- or antiaromatic due to destabilizing 1,3-interactions. Schleyer and co-workers predicted that the dication **5a**[17b] and **5b** are folded;[17b,c] likewise, dianion **6a**[18] does not have a square geometry.[18] MINDO/3[19] and ab initio calculations[17f] are in agreement that the planar D_{4h} structure **6a** is not a minimum. The instability of **6a** has been shown by MINDO[13c] and ab initio[18] calculations to result from Coulombic repulsion in the four-membered ring. According to Hess et al.'s ab initio calculations,[17f] the cyclobutadiene dianion has the C_s structure **6a′** in which the negative charge is delocalized at the allylic anion fragment and localized at the C-4 atom. Subsequent 6-31G(d) calculations have shown, however, that the C_s structure **6a′** corresponds to a saddle point on the potential energy surface of $C_4H_4^{2-}$, while the global minimum (**6a″**) has C_2 symmetry.[20]

5a'

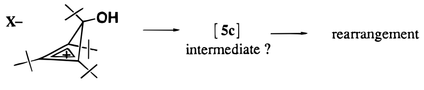


6a'



6a''

Attempts to generate the stable dication **5c** derived from tetra-*tert*-butylcyclobutadiene (**1c**) have failed; e.g., the reaction of hydroxy salt **8** with superacid giving instead some ring-expanded dications via a series of Wagner−Meerwein rearrangement.[2a]



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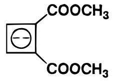
However, Olah and co-workers[21] succeeded in the unambiguous identification of the tetramethylcyclobutadiene dication **5b**. Bremer and Schleyer established the nonplanar structure by comparing the calculated chemical shifts[22] (which showed a pronounced dependence of the geometry) with experiment.[23]

Alkyl groups are not effective in stabilizing cyclobutadiene dianions.[24] Cyclic voltammetry of tetra-*tert*-butylcyclobutadiene (**1c**) showed no indication of the formation of the corresponding dication **5c** or dianion **6c**.[25] The oxidation was an irreversible one-electron process, and no waves attributable to redox reactions of the dication or dianion could be observed.



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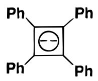

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A number of attempts to prepare derivatives of **6a** have been unsuccessful. However, Pettit and co-workers[23] provided some evidence for the intermediacy of **6a** itself by treatment of 3,4-dichlorocyclobutene with excess sodium naphthalide and quenching with MeOD. Cyclobutadiene dianions **11**[27] and **12**,[28] which bear suitable substituents like ester and phenyl groups to stabilize the negative charge, have been prepared. In both cases, only 40% of the negative charge was localized on the ring; the rest was distributed on the substituents. As the ring size decreases, the charge density per atom increases, and at high charge densities, dianions (even in solvent) may not be stable to electron loss. These observations indicate that the dianions **11** and **12** do not experience any "aromatic stabilization". Expected energy gain by delocalization of the negative charges in the aromatic system is offset by the electron repulsion in the dianion.

Lithium complexation is a well-known method for stabilizing anionic species.[29,30] In a study of $Li_2C_4H_4$ isomers, the symmetric dicapped D_{4h} structure (**7a**) was found to be 26.3 kcal/mol higher in energy than the dibridged ring-opened form (HF/6-31G(d)).[31] However, in Li_2-biphenylene the two forms must be close in energy (at least in solution).[32] Li_2-biphenylene opens to the dibridged form at 0 °C, while the Li_2-tetramethylbiphenylene retains the central four-membered ring even at room temperature.[32]

In this work, we focus on the tetramethyl and tetra-*tert*-butyl derivatives of cyclobutadiene and tetrahedrane. It is clear that the bulky *tert*-butyl groups play a favorable role (electronic or steric or both), since the parents are either extremely unstable (cyclobutadiene) or unknown (tetrahedrane).

Computational Methods

All geometries were fully optimized in the given symmetry at the HF/6-31G(d) and B3LYP/6-31G(d) levels.[33] Vibrational frequencies were calculated at the HF/6-31G(d) level to determine the nature of the stationary points as well as the zero-point and heat capacity corrections. Single-point calculations at the B3LYP/6-311+G(d) level on B3LYP/6-31G(d) geometries with HF/6-31G(d) zero-point corrections (scaled by 0.89

TABLE 1: Absolute Energies (hartrees), Zero-Point Energies (kcal/mol), and NICS Values (ppm) for Various Derivatives of Tetrahedrane, and Charged and Uncharged Cyclobutadiene Optimized at the HF/6-31G(d) and B3LYP/6-31G(d) Levels

		//HF/6-31G(d)		//B3LYP/6-31G(d)		
		HF/6-31G(d)	ZPE(NEV)	B3LYP/6-31G(d)	B3LYP/6-311+G(d)	NICS(0)(NICS(1))
$C_4H_4^{2+}$	D_{4h}	−152.905 42	41.56(1)	−153.853 97	−153.879 60	12.6(−10.4)
$C_4H_4^{2+}$	D_{2d}	−152.916 50	41.58(0)	−153.867 09	−153.892 51	−9.0
C_4H_4	D_{2h}	−153.641 17	41.68(0)	−154.675 46	−154.712 80	25.9(17.5)
C_4H_4	T_d	−153.597 89	40.68(0)	−154.636 69	−154.670 68	−48.3
C_4H_4	C_{2v}	−153.603 90	40.16(0)	−154.647 78	−154.685 10	
C_4H_4 bi	D_{4h}	−153.688 65	38.70(0)	−154.674 25	−154.709 65	
$C_4H_4^{2-}$	D_{4h}	−153.245 72	34.40(3)	−154.353 08		−25.5(−9.4)
$C_4H_4^{2-}$	C_{2h}	−153.280 54	34.93(1)	−154.393 65		−15.8(−9.6)
$C_4H_4^{2-}$	C_2	−153.282 18	35.77(0)	(a)		
$C_4Me_4^{2+}$	S_4	−309.212 60	114.65(1)	−311.314 38	−311.369 91	10.3(−10.6)
$C_4Me_4^{2+}$	D_{2d}	−309.220 35	115.36(0)	−311.317 12	−311.372 75	−0.8
C_4Me_4	D_{2h}	−309.814 12	116.78(0)	−311.972 29	−312.038 30	19.4(11.9)
C_4Me_4	T_d	−309.762 03	117.17(0)	−311.922 29	−311.985 35	−47.2
$C_4Me_4^{2-}$	D_{2d}	−309.444 04	107.63(2)	−311.695 30		−14.8
$C_4Me_4^{2-}$	C_{2h}	−309.465 10	109.36(1)	−311.709 07		−17.3(−11.3)
$C_4Me_4^{2-}$	C_2	−309.467 45	109.96(0)	(a)		
C_4Me_3H	C_s	−279.771 93	98.03(0)	−272.649 24	−272.708 42	19.5(12.8)
C_4Me_3H	C_s	−270.734 90	96.06(1)	−272.615 18	−272.674 54	−13.9
C_4Me_3H bi	C_s	−270.810 48	94.88(2)	−272.640 87	−272.698 37	
C_4-*t*-Bu_4^{2+}	D_{2d}	−777.665 37	344.57(1)	−782.121 82	−783.270 49	−16.6
C_4-*t*-Bu_4^{2+}	D_2	−777.667 14	344.51(1)	−783.122 44	−783.270 98	−19.1
C_4-*t*-Bu_4^{2+}	C_2	−777.668 65	345.01(0)	−783.124 10	−783.272 74	−17.2
C_4-*t*-Bu_4	D_2	−778.156 42	346.08(0)	−783.680 72	−783.841 13	17.9
C_4-*t*-Bu_4	T_d	−778.166 87	344.35(1)	−783.682 67	−783.840 62	
C_4-*t*-Bu_4	T	−778.170 05	344.64(0)	−783.683 45	−783.841 41	−46.8
C_4-*t*-Bu_4^{2-}	D_{2d}	−777.859 69	337.42(2)	−783.479 38		−11.6
C_4-*t*-Bu_4^{2-}	C_2	−777.882 84	339.11(0)	−783.487 24		−12.4
C_4-*t*-Bu_3H	C_1	−622.058 21	269.62(0)	−626.453 85	−626.584 14	19.6
C_4-*t*-Bu_3H	C_s	−622.023 47	267.71(1)	−626.421 04	−626.551 94	−4.1
C_4-*t*-Bu_3H bi	C_s	−622.100 70	267.29(0)	−626.449 00	−626.577 54	
CH_4	T_d	−40.195 17	29.98(0)	−40.518 39	−40.528 07	
C_2H_4	D_{2h}	−78.031 72	34.37(0)	−78.587 46	−78.608 35	
C_2H_6	D_{3d}	−79.228 75	50.05(0)	−79.830 42	−79.848 38	
CMe_4	T_d	−196.333 82	107.09(0)	−197.773 09	−197.815 98	
$Li_2C_4H_4$	D_{4h}	−168.605 13	43.64(0)	−169.824 86	−169.864 41	98.6[b]/−23.7
$Li_2C_4Me_4$	C_{2h}	−324.723 27	118.09(0)	−327.068 74	−327.139 73	98.8[b]/−22.0
Li_2C_4-*t*-Bu_4	D_2	−793.067 51	347.14(1)	−798.784 16	(c)	97.7[b]/−23.4
Li_2C_4-*t*-Bu_4	C_2	−793.067 94				
Li	K_h	−7.431 37	0.0	−7.490 98	−7.491 33	
Li^+	K_h	−7.235 54	0.0	−7.284 54	−7.284 92	95.4[b]
MeLi	C_{3v}	−47.015 54	22.28(0)	−47.401 12	−47.414 79	90.4[b]

[a] Optimizes to C_{2h} symmetry. [b] ^{7}Li absolute shielding in ppm. [c] No SCF convergence.

to take account of known inadequacies in frequencies calculated at this level[34]) constitute our "standard" level.

The B3LYP/6-31G(d) method has been shown to yield accurate geometries which are comparable to the MP2/6-31G(d) level.[35] Molecular plots of the relevant structures are given in Figures 1. Total energies (hartrees) and zero-point energies (kcal/mol) are given in Table 1 while Cartesian coordinates of all species are provided as Supporting Information.

TABLE 2: Relative Energies (kcal/mol) for Cyclobutadiene (1a) and Tetrahedrane (2a) C_4H_4 Species

			//B3LYP/6-31G(d)		
		//HF/6-31G(d) HF/6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-311+G(d)	+ZPC/ 6-31G(d)
C_4H_4 (**1a**)	D_{2h}	0.0	0.0	0.0	0.0
C_4H_4 (**2a**)	T_d	27.2	24.3	26.4	25.4
$C_4H_4^{2-}$	D_{4h}	248.1	202.3		195.7
$C_4H_4^{2-}$	C_{2h}	226.3	176.8		170.7
$C_4H_4^{2-}$	C_2	225.3			
$C_4H_4^{2+}$	D_{4h}	462.2	515.4	522.8	522.7
$C_4H_4^{2+}$	D_{2d}	454.7	507.2	514.7	514.6

Results and Discussion

Relative energies of $C_4R_4^n$, $n = 0, -2, +2$, species are given in Table 2 for R = H, Table 3 for R = Me, and Table 4 for R = *t*-Bu. Corresponding geometries (including dilithio compounds) are given in Figures 1 and 2. For the parent C_4H_4 system, many higher level calculations have been reported.[36] We include data here for comparison. At our standard level, cyclobutadiene is favored over tetrahedrane by 25.4 kcal/mol, in good agreement with a G2 value of 26.0 kcal/mol.[36]

We have explored two main effects: (1) the effect of adding or removing two electrons from cyclobutadiene, and (2) the effect of replacing hydrogens with methyl or *tert*-butyl groups. If two electrons are added to C_4H_4, the $4\pi + 2$ aromaticity of the four membered ring does not overcome the electron repulsion which destabilizes the D_{4h} structure (three imaginary frequencies, HF/6-31G(d)). Favorable distortions lead to a C_{2h} geometry with one imaginary frequency and finally to the lowest energy C_2 structure. These results are identical to those obtained by van Zandwijk et al.[20] When the C_2 structure was optimized at the B3LYP/6-31G(d) level, the more symmetrical C_{2h} structure was obtained. We encountered problems when we calculated the dianion with the 6-311+G(d) basis set since generally some of the highest occupied orbital energies of the dianion are positive (unbound). As a consequence, dianion computations with limited basis sets provide artifical descriptions

TABLE 3: Relative Energies (kcal/mol) for Cyclobutadiene (1b) and Tetrahedrane (2b) C_4Me_4 Species

			//B3LYP/6-31G(d)		
		//HF/6-31G(d) HF/6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-311+G(d)	+ZPC/ 6-31G(d)
C_4Me_4 (**1b**)	D_{2h}	0.0	0.0	0.0	0.0
C_4Me_4 (**2b**)	T_d	32.7	31.4	33.2	33.6
$C_4Me_4^{2-}$	D_{2d}	232.2	173.8		165.6
$C_4Me_4^{2-}$	C_{2h}	219.0	165.2		158.5
$C_4Me_4^{2-}$	C_2	217.5			
$C_4Me_4^{2+}$	D_{2d}	372.6	411.1	417.6	416.3

TABLE 4: Relative Energies (kcal/mol) for Cyclobutadiene (1c) and Tetrahedrane (2c) C_4-*t*-Bu_4 Species

			//B3LYP/6-31G(d)		
		//HF/6-31G(d) HF/6-31G(d)	B3LYP/ 6-31G(d)	B3LYP/ 6-311+G(d)	+ZPC/ 6-31G(d)
C_4-*t*-Bu_4 (**1c**)	D_2	0.0	0.0	0.0	0.0
C_4-*t*-Bu_4	T_d	−6.6	−1.2	0.3	−1.0
C_4-*t*-Bu_4 (**2c**)	T	−8.6	−1.7	0.2	−1.5
C_4-*t*-Bu_4^{2-}	D_{2d}	186.2	126.3		118.5
C_4-*t*-Bu_4^{2-}	C_2	171.7	121.4		115.1
C_4-*t*-Bu_4^{2+}	D_{2d}	308.1	350.7	358.1	356.7
C_4-*t*-Bu_4^{2+}	D_2	307.0	350.3	357.8	356.4
C_4-*t*-Bu_4^{2+}	C_2	306.1	349.3	356.7	355.7

since such species are not stable toward electron loss in isolation. The addition of diffuse functions to the basis set resulted in orbitals with very small energies which acquired significant population.[37] In effect, these were describing Rydberg states. Therefore, we chose to compute illustrative energies of dianions without diffuse functions, i.e., at B3LYP/6-31G(d)//B3LYP/6-31G(d) + ZPC/6-31G(d). At this standard level for dianions, the C_{2h} structure is 170.7 kcal/mol above cyclobutadiene (Table 2).

The removal of two electrons from cyclobutadiene does not result in such problems. The symmetric D_{4h} cyclobutadiene dication (**5a**) is a transition structure; the folded D_{2d} minimum is 8.1 kcal/mol lower in energy. The nonplanar structure of the dication is due to the increase in both the 1,3-homoallylic bonding interactions and the greater mixing of orbitals.[17b−d,22] The energy difference between the D_{4h} and D_{2d} structure is 9.6 kcal/mol at the MP4/6-31G(d)//6-31G(d) level.[22] The energy of the D_{2d} dication (**5a**) is 514.0 kcal/mol above neutral cyclobutadiene (**1a**).

The D_{2d} symmetry tetramethyl dianion (**6b**) has four equivalent C−C ring bonds (1.467 Å); the ring carbons are out of plane by 0.038 Å. The D_{2d} symmetry structure has two imaginary frequencies and, when the symmetry is relaxed, distorts into a C_{2h} structure where the ring carbons are significantly more pyramidal (two adjacent methyl groups are up and two down). At the HF/6-31G(d) level, the C_{2h} structure has one imaginary frequency which leads to a C_2 symmetry trapezoidal structure with one long C−C bond (1.570 Å), and one short (1.378 Å) and two intermediate C−C bonds (1.473 Å). The charge is localized with very pyramidal environments on the two carbons forming the longest bond. The C_2 structure optimizes back to C_{2h} symmetry at the B3LYP/6-31G(d) level. Methyl groups stabilize the dianion relative to cyclobutadiene because of charge delocalization over a greater number of atoms. At our standard level, the C_{2h} symmetry structure of $C_4Me_4^{2-}$ is 158.5 kcal/mol less stable than neutral tetramethylcyclobutadiene (compared to 170.7 kcal/mol in the parent). The four ring carbons have a total negative charge of 0.33 e^- in the tetramethyl C_{2h} dianion compared to 1.29 e^- in the parent (B3LYP/6-31G(d)).

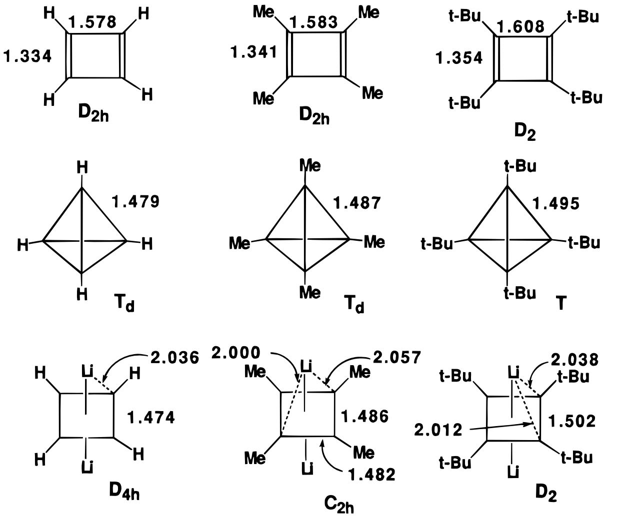


Figure 1. Calculated geometric parameters cyclobutadiene (**1a**) and tetrahedrane (**2a**) and tetramethyl (**1b, 2b**) and tetra-*tert*-butyl (**1c, 2c**) derivatives at B3LYP/6-31G(d). Also included are the dilithiocyclobutadiene species **7a**−**c**.

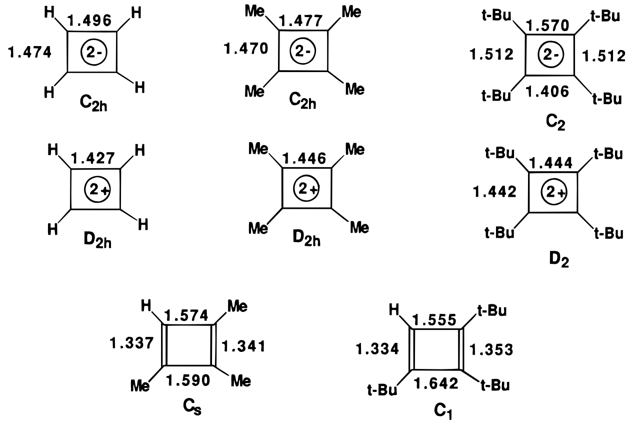


Figure 2. Calculated geometric parameters for dianions (**6a**) and dications (**5a**) of cyclobutadiene and tetramethyl (**5b, 6b**) and tetra-*tert*-butyl (**5c, 6c**) derivatives at B3LYP/6-31G(d).

The D_{2d} symmetry tetramethyl dication (**5b**)[17b−d,22] is similar to the unsubstituted D_{2d} cyclobutadiene dication with the exception that the methyl groups stabilize the positive charges significantly, much more than in the dianion. Relative to the cyclobutadiene dication, the methyl groups stabilize the charge in **5b** by 98.3 kcal/mol (Tables 2 and 3; 514.6−416.3 kcal/mol).

Bulky *tert*-butyl groups are important in determining the lowest-energy structure. The four *tert*-butyl groups are staggered in tetra-*tert*-butylcyclobutadiene (**1c**) and force the ring carbons out of plane by 0.054 Å, thus, reducing the symmetry from D_{2h} to D_2 (Figure 3). The two sets of ring C−C bonds (1.354 and 1.608 Å) differ by 0.254 Å which confirms the previously suggested (but not directly determined)[15] distortion in the low-temperature X-ray structure. While the C−C bond of 1.608 Å is not close to highly elongated C−C bonds,[38] it may be the longest C−C bond between two sp^2 carbons. Compared to tetramethylcyclobutadiene (**1b**), the C=C bond in tetra-*tert*-butylcyclobutadiene (**1c**) is 0.013 Å longer and the C−C bond 0.025 Å longer (Figure 1).

At the HF/6-31G(d) level, T_d-symmetry tetra-*tert*-butyltetrahedrane has one imaginary frequency (74i); further optimization leads to a *T*-symmetry structure. This is 2.0 kcal/mol lower in energy at HF/6-31G(d) but only 0.5 kcal/mol lower than T_d at

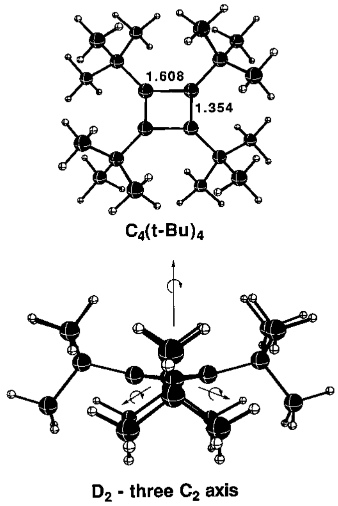


Figure 3. Molecular plot of tetra-*tert*-butylcyclobutadiene (**1c**) in D_2 symmetry.

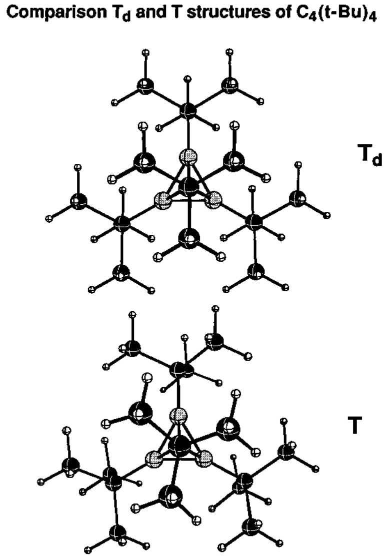


Figure 4. Molecular plot of tetra-*tert*-butyltetrahedrane (**2c**) in T_d and T symmetry.

our standard level (Figure 4). Mislow[39] had previously predicted the favorable $T_d \rightarrow T$ distortion based on force field calculations, though the computed energy difference (2−6 kcal/mol) is larger than that found here. The driving force behind the distortion is relief of steric repulsion between methyl groups on different *tert*-butyl groups. In the T_d symmetry structure, there are 12 nonbonded H···H interactions of 2.25 Å which are reduced to 12 H···H interactions of 2.43 Å in the T-symmetry structure. Our computed C−C cage distances in C_4-*t*-Bu_4 are 1.495 Å, which can be compared to the X-ray value of 1.485 Å.[39] The symmetric a_1 C−C cage stretching mode is predicted to be 1638 cm^{-1} (after scaling with 0.89 factor) which is in good agreement with the experimental value of 1683 cm^{-1}.[41]

At our standard level, tetra-*tert*-butylcyclobutadiene (**1c**) is actually 1.5 kcal/mol more stable than tetra-*tert*-butyltetrahedrane (**2c**) in the gas phase. Our calculations may overestimate the stability of (**2c**) relative to **1c** since heating is known[2] to produce **1c** from **2c**.

Entropy effects may be important since the tetrahedron cage is expected to be more rigid than the cyclobutadiene ring. However, calculating entropies of C_4-*t*-Bu_4 isomers are problematic due to the treatment of methyl rotations as normal frequencies. Therefore, we estimated the effect of entropy by subtracting the contribution of the 12 methyl torsions in both molecules. When this is done, the entropy of tetra-*tert*-butylcyclobutadiene (**1c**) is 4 eu larger than that of tetra-*tert*-butyltetrahedrane (**2c**) which contributes −1.2 kcal/mol to the free energy difference at 298 K. Our data thus show **1c** and **2c** to have nearly the same stability.

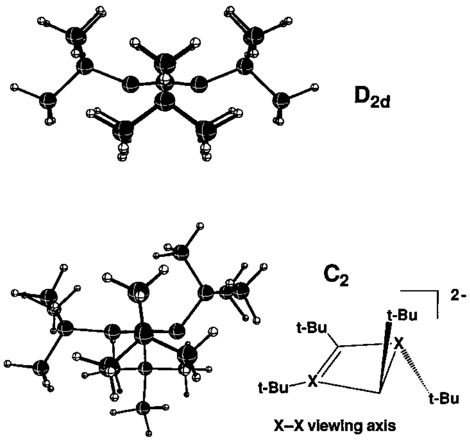


Figure 5. Molecular plot of tetra-*tert*-butylcyclobutadiene dianion (**6c**) in C_2 symmetry.

The D_{2d}-symmetry dianion, derived by adding two electrons to **1c**, was calculated to be 118.5 kcal/mol higher in energy than tetra-*tert*-butylcyclobutadiene. The D_{2d} geometry had two imaginary frequencies at the HF/6-31G(d) level and led to a lower energy structure in C_2 symmetry with zero imaginary frequencies (total of 0.51 e^- on ring carbons at B3LYP/6-31G(d)). Unlike the parent and tetramethyl dianions in C_2 symmetry, the B3LYP/6-31G(d) optimization of the *tert*-butyl-substituted dianion did not rearrange back to a higher symmetry structure (Figure 5). However, the tetra-*tert*-butyl $D_{2d} - C_2$ difference of 14.5 kcal/mol at HF/6-31G(d)//6-31G(d) is reduced to only 4.9 kcal/mol at B3LYP/6-31G(d)//B3LYP/6-31G(d).

Removing two electrons from **1c** yields a dication of D_{2d} symmetry, structure **5c**, which is 356.7 kcal/mol higher in energy than **1c** (Table 4). When the imaginary frequency computed for the D_{2d} geometry is followed, a D_2 symmetry structure is obtained, 1.1 kcal/mol lower at the HF/6-31G(d) level. The D_2 structure has one imaginary frequency which leads to the C_2 minimum (zero imaginary frequencies), 0.9 kcal/mol lower in energy. The B3LYP/6-31G(d) results were similar: the three structures (D_{2d}/D_2/C_2) are separated by only 1 kcal/mol. The lower symmetry is due to the reduction of the nonbonded repulsion between methyl hydrogens on different *tert*-butyl groups. There are four H···H separations of 2.10 Å between *tert*-butyl groups in the D_{2d} structure. This is reduced to four H···H separations of 2.12 Å in the D_2 symmetry structure and to two separations of 2.27 Å in the C_2 symmetry structure.

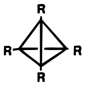
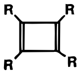
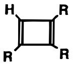
While the parent dianion and dication have not been observed, the tetramethyl dication has been characterized in superacid media.[21,22] Fox et al.[25] studied the electrochemistry of the *tert*-butyl derivative in acetonitrile. The monoanion and monocation radicals were observed, but not the dianion or dication. Solvation will clearly stabilize charged relative to neutral species. In order to determine the magnitude of these effects in acetonitrile, we used the SM5.4/AM1 model[42,43] on fixed B3LYP/6-31G(d) geometries. In addition, we computed the radical anion in the fixed D_{2d} geometry of the dianion at the B3LYP/6-31G(d) level and computed the SM5.4/AM1 free energy of solvation (Table 5). For these rough comparisons, we ignored zero-point, heat capacity, and entropy corrections and simply added the SM5.4/

TABLE 5: Calculated SM5.4/A Solvation Energies (kcal/mol) and Estimated Stability of Tetra-*tert*-butyltetrahedrane (2c) and Neutral and Charged Tetra-*tert*-butylcyclobutadiene in Acetonitrile

		gas phase energy diff	solvation energy SM5.4A (aceonitrile)[a]	est rel free energy[b]
C_4-*t*-Bu_4 (**1c**)	D_2	0.0	−9.2	0.0
C_4-*t*-Bu_4	T_d	−1.0	−8.5	−0.3
C_4-*t*-Bu_4 (**2c**)	T	−1.5	−8.2	−0.5
C_4-*t*-Bu_4^{2-}	D_{2d}	118.5	−167.4	−39.7
C_4-*t*-Bu_4^{2-}	C_2	115.1	−162.2	−37.9
C_4-*t*-Bu_4^{2+}	D_{2d}	356.7	−150.0	197.5
C_4-*t*-Bu_4^{2+}	D_2	356.4	−150.2	197.0
C_4-*t*-Bu_4^{2+}	C_2	355.4	−150.0	196.2
C_4-*t*-Bu_4^{-} [c]	D_{2h}	18.8	−51.0	−23.0

[a] Reference 43. [b] Obtained by adding gas-phase energy difference to solvation energy and shifting (by 9.2 kcal/mol) to give the D_2 symmetry tetra-*tert*-butylcyclobutadiene a value of zero. [c] Calculation on radical anion performed on fixed dianion geometry of D_{2h} symmetry.

TABLE 6: Heats of Formation (kcal/mol) Calculated from Isodesmic Reactions at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) Level[a]

	R = H		R = Me		R = *t*-Bu	
	0 K	298 K	0 K	298 K	0 K	298 K
	130.4	133.2[b]	96.1	102.7	16.2	31.9[e]
	105.0	107.8[c,d]	62.5	69.2	17.7	33.3
			72.2	77.8	23.4	35.7

[a] Experimental heats of formation (ΔH_f) in kcal/mol at 298 K; CH_4, −17.9; C_2H_4, 12.5; C_2H_6, −20.0; neopentane, −40.1. Heat capacity corrections to 298 K were made using unscaled HF/6-31G(d) vibrational frequencies. [b] G2 value is 127.8 kcal/mol.[36] [c] G2 value is 101.8 kcal/mol.[36] For an alternative heat of formation for cyclobutadiene of 107.3 kcal/mol see: Hrouda, V.; Roseselová, M.; Bally, T. *J. Phys. Chem. A* **1997**, *101*, 3925, footnote 49. [d] An experimental value of 114 ± 11 kcal/mol using photoacoustic calorimetry has recently been reported. See: Deniz, A. A.; Peters, K. S.; Snyder, G. J. *Science* **1999**, *286*, 1119. [e] Experimental estimate is 6.2 kcal/mol (ref 2a).

AM1 free energies of solvation to B3LYP/6-311+G(d) relative energies (B3LYP/6-31G(d) for anions and dianions). Certainly, the stability of the anion is underestimated since no optimization was carried out. However, it is interesting to note that the stabilities of the anion and dianion are very similar. Of course, the presence of Li^+ or other counterions will stabilize such species electrostatically.

Heats of Formation. Heats of formation of cyclobutadiene and tetrahedrane, computed at the G2 level with eq 1 and related isodesmic and homodesmotic reactions, are 101.8 ± 1 and 127.8 ± 1 kcal/mol at 298 K, respectively. Using similar isodesmic reactions, we have calculated heats of formation of methyl and *tert*-butyl derivatives (Table 6). The isodesmic reaction for C_4H_4 is given in eq 1. For C_4Me_4 and $C_4(t\text{-}Bu)_4$ we added reactions 1 and 2 to obtain reaction 3.

$$C_4H_4 + 4CH_4 \rightarrow 2C_2H_4 + 2C_2H_6 \qquad (1)$$

$$C_4R_4 + 4CH_4 \rightarrow C_4H_4 + 4RCH_3\ (R = Me,\ t\text{-}Bu) \qquad (2)$$

$$C_4R_4 + 8CH_4 \rightarrow 2C_2H_4 + 2C_2H_6 + 4RCH_3 \qquad (3)$$

For R = CH_3, RCH_3 is ethane and for R = *t*-Bu, RCH_3 is neopentane. The calculated heats of formation are given in Table 6. The calculated heats of formation are 5−6 kcal/mol greater than the G2 values for the parent cyclobutadiene (**1a**) and tetrahedrane (**2a**). We would expect the data for R = Me (**1b** and **2b**) and R = *t*-Bu (**1c** and **2c**) in Table 6 to also be about 5−6 kcal/mol too high (provided the G2 values are correct) since the discrepancy should be transferable. Maier,[2] in his review paper, gives an estimate of ΔH_f° for tetra-*tert*-butyltetrahedrane (**1c**) of 6.2 ± 2.1 kcal/mol based upon a heat of combustion of −3099.8 ± 1.8 kcal/mol and a heat of sublimation of 17.1 ± 0.8 kcal/mol. Our value is 25.7 kcal/mol larger.

Using group additivity increments, one can compute a heat of formation of tetra-*tert*-butyltetrahedrane free from exo-substituent interactions of 16.6 kcal/mol.[44] The 15.3 kcal/mol higher computed heat of formation (Table 6) can be attributed to the steric repulsion between the *tert*-butyl groups.

The reaction in eq 4 was used to compute heats of formation for

$$C_4R_3H + 7CH_4 \rightarrow 2C_2H_4 + 2C_2H_6 + 3RCH_3 \qquad (R = Me,\ t\text{-}Bu) \quad (4)$$

C_4Me_3H and C_4-*t*-Bu_3H. The heats of formation in Table 6 were used to evaluate reaction energies in eqs 2 and 5. Reaction 2, which compares the stabilizing effect of substituent R relative to that of hydrogen, is 30.2 kcal/mol endothermic for R = Me (**1b**) and 14.4 kcal/mol exothermic for R = *t*-Bu (**1c**). Reaction 5, which shows the effect of replacing one R group of C_4R_4 with

$$^3/_4C_4R_4 + {}^1/_4C_4H_4 \rightarrow C_4R_3H\ (R = Me,\ t\text{-}Bu) \qquad (5)$$

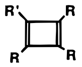
hydrogen, is 1.0 kcal/mol exothermic for R = Me (**1b** → C_4Me_3H) and 16.2 kcal/mol exothermic for R = *t*-Bu (**1c** → C_4-*t*-Bu_3H). The larger exothermicicity for R = *t*-Bu compared to R = Me is mainly due to relief of steric repulsion.

Methyl substitution stabilizes C=C double bonds more than C−C single bonds.[44a] Thus, the 25.4 kcal/mol energy difference (**1a** → **2a**) between cyclobutadiene and tetrahedrane (Table 6) is increased to 33.5 kcal/mol (**1b** → **2b**). In the tetramethyl derivatives, these small alkyl groups thus have the opposite effect than *tert*-butyl groups.

Automerization. Automerization of cyclobutadiene, the interconversion of the equivalent rectangular forms, has been of great interest,[5a,45−54] also due to the possibility that heavy atom tunneling (HAT) may occur.[45] The activation enthalpy of automerization in cyclobutadiene has been determined from vibrational splitting in matrix isolation studies to be about 5 kcal/mol.[5a] Carpenter[45] calculated that the rate of interconversion below 0 °C was faster via HAT than over the classical barrier. More refined calculations[46−49] suggest that the rate of automerization for temperatures close to absolute zero is 2.5×10^{11} s^{-1}.[48] However, further experimental work by Michl and coworkers[49] showed that, while HAT undoubtedly takes place, the rate cannot be as fast as computed by theory. The classical activation energy (E_a) for automerization has been calculated by a number of different procedures. Reasonably reliable methods give activation energies between 6 and 10 kcal/mol.[47,48,52]

Petersson et al.[53] calculated that tetrafluorocyclobutadiene (C_4F_4) has a nonplanar (C_{2h}) ground state. Their analysis of the IR spectrum revealed no evidence of automerization. They suggested that the large displacements required for exchanging forms with fluorine substituents might inhibit HAT.

TABLE 7: Experimental and Calculated Automerization Activation Parameters (kcal/mol) for Cyclobutadiene and Derivatives

		E_a (calculated)	
	$\Delta H^‡$ (exptl)	this work[a]	other[b]
R′ = R = H	5[c]	3.8	6−10
R′ = R = F	*d*		
R′ = H, R = Me		6.3	
R′ = H, R = *t*-Bu	<2.5[e,f]	4.1	
R′ = SiMe$_3$, R = *t*-Bu	3[e,g]		
R′ = SiMe$_2$Ph, R = *t*-Bu	4.5 ± 0.2[e,g]		
R′ = CHCH$_3$OSiMe$_3$, R = *t*-Bu	5.3 ± 0.2[g]		
R′ = GeMe$_3$, R = *t*-Bu	3.6[h]		

[a] UB3LYP/6-311+G(d)//UB3LYP/6-31G(d). Zero-point energy not included. [b] References 47, 48, and 52. [c] Reference 5a. [d] Automerization not observed. Reference 53. [e] Free energy of activation, $\Delta G^‡$. [f] Reference 55. [g] Reference 2d. [h] Reference 2e.

Maier and co-workers[2f−i,55] used the temperature dependence of ^{13}C NMR chemical shifts to extract the $\Delta G^‡$ of automerization for several derivatives of cyclobutadiene. These systems, which contain three *tert*-butyl groups and a different fourth substituent, all had free energies of activation between 2 and 6 kcal/mol (Table 7). Since entropy effects are expected to be small, $\Delta G^‡$ and $\Delta H^‡$ are expected to be similar.

We looked at automerization in the two derivatives, C$_4$Me$_3$H and C$_4$-*t*-Bu$_3$H, where experimental data is available for the latter (Table 7). The two C−C single bonds (1.555 and 1.642 Å) of C$_4$-*t*-Bu$_3$H (C_1 symmetry) are quite different while the average (1.598 Å) is only slightly shorter than that for the tetra-*tert*-butyl derivative (1.608 Å). In order to relieve steric congestion, the single C−C bond adjacent to hydrogen is compressed. Since the reaction path for automerization must interconvert the double and single bonds, we chose to optimize the transition state with a plane of symmetry including the C−H bond and the opposite C−R bond (R = H, Me, *t*-Bu). At our standard level, the C_s structures are 16.9 (C$_4$H$_4$; C_{2v} symmetry), 19.4 (C$_4$Me$_3$H), and 18.5 (R = C$_4$-*t*-Bu$_3$H) kcal/mol higher than the cyclobutadiene derivative.

Interestingly, the C$_4$H$_4$ C_{2v} structure is a minimum rather than a transition state, even at higher levels of theory (B3LYP/6-311+G(d,p) and CASSCF(4,4)[56]). The transannular C−C bond in C$_4$R$_3$H increases from 1.651 to 1.713 to 1.836 Å as R changes from R = H to R = Me to R = *t*-Bu. Dewar has calculated the same intermediate at the MINDO/3 level as part of the cyclobutadiene PES.[16b] We are currently investigating how the bicyclic form might be stabilized. However, the bicyclic intermediate/transition state is too high in energy to be involved in the automerization process, which is known to occur with much smaller activation barriers (Table 7).

When we used an unrestricted wave function to determine the open-shell biradical structure for C$_4$R$_3$H, R = H, Me, *t*-Bu, we were able to find much lower-energy structures. While it is well recognized that the unrestricted wave function leads to deviations of the $\langle S^2 \rangle$ values from the value of zero expected for singlet states, open-shell singlet calculations by UDFT do yield reasonable descriptions of biradicals.[57,58] For example, Houk and co-workers[58] have reported success in studying reactions involving biradicals using the UB3LYP method. We optimized the open-shell biradical structures at UB3LYP/6-31G(d) and carried out single-point calculations at the UB3LYP/6-311+G(d) level. Zero-point corrections were not included. Thus computed, the activation energy for automerization in cyclobutadiene was 3.8 kcal/mol, in reasonable agreement with high-level theory[47,48,52] but about 4 kcal/mol lower than the best experimental estimates (see above).[46,47,51]

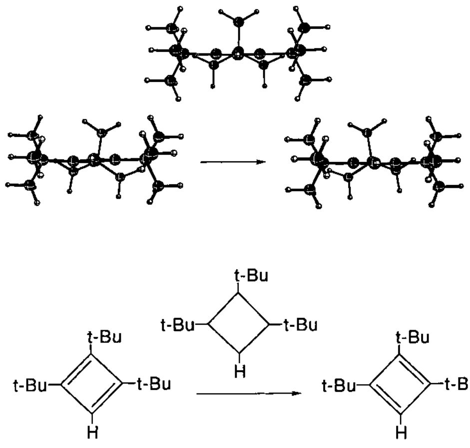
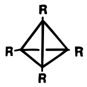
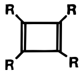
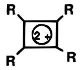
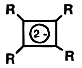
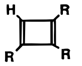


Figure 6. Molecular plots of reactant, transition state, and product in the automerization of tri-*tert*-butylcyclobutadiene, C$_4$-*t*-Bu$_3$H.

TABLE 8: Comparison of NICS(0) Values (ppm) at the GIAO/HF/6-31G(d)//B3LYP/6-31G(d) Level

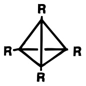
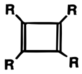
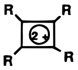
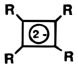
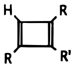
	R = H	R = Me	R = *t*-Bu
	−48.3 (T_d)	−47.2 (T_d)	−46.8 (T)
	25.9 (D_{2h})	19.3 (D_{2h})	17.9 (D_2)
	−9.0 (D_{2d})	−0.8 (D_{2d})	−17.2 (C_2)
	−15.8 (C_{2h})	−17.3 (C_{2h})	−12.4 (C_2)
		19.5 (C_s)	19.6 (C_1)

The calculated barriers for automerization for R = Me and R = *t*-Bu are 6.3 and 4.1 kcal/mol, respectively. The latter value is in reasonable agreement with an experimental free energy of activation of 2.5 kcal/mol.[55] Figure 6 illustrates the motion required during the transformation.

Magnetic Properties. Magnetic criteria for aromaticity/antiaromaticity[54,59−64] include (1) anomalous proton chemical shifts, (2) large magnetic anisotropies, (3) diamagnetic/paramagnetic susceptibility exaltation, and (4) nucleus-independent chemical shifts (NICS).[63,64] We computed the magnetic properties of cyclobutadiene and tetrahedrane derivatives using the GIAO method[62] with the HF/6-31G(d) basis set at the B3LYP/6-31G(d) optimized geometries.

NICS values (Table 8), which are now widely used as a measure of aromaticity/antiaromaticity,[63,64] were obtained by calculating absolute NMR shieldings at the ring centers (cage centers for tetrahedranes). The large negative NICS(0) values in tetrahedrane, which is due to the shielding of the nearby internal CC and external bonds, are not affected by substituents. On the other hand, the positive (antiaromatic) NICS value of cyclobutadiene decreases as hydrogens are replaced with methyl and *tert*-butyl substituents. For the cyclobutadiene dication and dianion systems, all the NICS(0) values are negative consistent with a $4\pi + 2$ electron systems. The small value (−0.8 ppm) for C$_4$Me$_4$$^{2+}$ (Table 8) seems out of line due to deshielding effects of the external CH$_3$ groups. In contrast to the doubly charged species, the cyclobutadienes all have relatively large

TABLE 9: Calculated (GIAO/HF/6-31G(d)//B3LYP/6-31G(d)) and Experimental ^{13}C−Ring Chemical Shifts (ppm)[a]

	R = H		R = Me		R = *t*-Bu	
	calc(PG)[b]	exptl	calc(PG)[b]	exptl	calc(PG)[b]	exptl
	−26.2 (T_d)		−10.0 (T_d)		−0.7 (T)	9.27[c]
	139.1 (D_{2d})		140.3 (D_{2h})		162.4 (D_2)	152.7[d]
	180.0 (D_{2d})	182.1[e]	218.0 (D_{2d})	207.9[f]	184.0[g] (C_2)	
	85.6 (C_{2h})		81.3 (C_{2h})		103.2[g] (C_2)	
			(C_s) 128.6 (CH) 147.4 (CR)[g] 136.3 (CR′)		(C_1) 130.7 (CH) 156.8 (CR)[g] 148.6 (CR′)	 126.2 (CH)[h] 151.4 (CR)[h] 144.7 (CR′)[h]

[a] Chemical shift (δ) = 200.0 − absolute shielding. [b] The point group (PG) of the species is given in parentheses. [c] Reference 2a. [d] Reference 3. [e] For 1,2-diphenylcyclobutadiene dication. Reference 22. [f] Reference 22. [g] Average of ring carbons. [h] Reference 3.

positive NICS(0). The values in C_4R_3H indicate a similar degree of antiaromaticity as found in C_4R_4.

Chemical shifts (^{13}C and ^{1}H) were obtained relative to the calculated absolute shieldings of tetramethylsilane (TMS) in T symmetry (^{13}C, 200.0; ^{1}H, 32.6 ppm). While the calculated ^{13}C NMR chemical shifts in Table 9 may change at better levels of theory and with relative scaling,[65] even the small basis employed here (HF/6-31G(d)) should suffice for relative trends of R = H, Me, *t*-Bu. Indeed, all the computed ^{13}C shifts show an acceptable error at ±10 ppm vs the available experimental data.

The calculated ^{13}C chemical shift in the parent dication (180.0 ppm) is close to an estimate[22] (182.1 ppm) obtained from the 1,2-diphenylcyclobutadiene dication. However, the calculated chemical shift for the ring carbon in the tetramethyl dication (**5b**) derivative (218.1 ppm) is about 10 ppm larger (downfield) than the experimental value (207.9 ppm).[66] ^{13}C experimental chemical shifts are also available for C_4-*t*-Bu_3H. The calculated values are about 5 ppm larger than experimental values (Table 9).

Comparing the calculated ^{1}H chemical shift of cyclobutadiene (5.8 ppm, GIAO/B3LYP/6-311+G(d,p)) with the experimental olefinic ^{1}H chemical shift of reference compounds (cyclobutadiene to cyclobutene (5.8 → 6.0 ppm) and benzene to cyclohexene (7.3 → 5.6 ppm)) indicates a much smaller downfield shift than the upfield shift found for benzene. Wüllen and Kutzelnigg[67] attributed their calculated (MC-IGLO) upfield shift of ^{1}H in cyclobutadiene relative to olefins to a paramagnetic ring current, but the difference is small. Our "disected NICS"[63f,p] analysis (to be published in detail elsewhere) reveals that the cyclobutadiene paramagnetic π ring current does shield the protons in cyclobutadiene appreciably, but is counterbalanced by diamagnetic σ contributions of the CC and CC single bonds.

The cyclobutadiene ^{1}H chemical shift has been measured[3] for C_4R_3H, R = *t*-Bu (5.4 ppm), which can be compared to a calculated value of 5.5 ppm (GIAO/6-31G(d)//B3LYP/6-31G(d)). As R is changed in C_4R_3H from R = H to R = Me to R = *t*-Bu, the calculated ^{1}H chemical shift remains essentially constant (5.6, 5.5, 5.5 ppm).

Lithium-Capped Dianions. The addition of lithium to a ring system is an effective means of stabilizing the corresponding anionic or dianionic system.[68] The lithium cations may coordinate to a single atom (η^1) or may coordinate above a ring (η^n).[69] In the $C_4R_4^{2-}$ dianions, the most stable coordination site for two Li^+ cations is above and below the ring.[31] As opposed to the ring-opened C_2-symmetry global minimum of $C_4H_4^{2-}$, the lowest-energy $Li_2C_4H_4$ structure has both lithiums on a 4-fold axis in D_{4h} symmetry.[31,70] The methyl groups lower the symmetry of $Li_2C_4Me_4$ to C_{2h}, but the lithium−ring carbon distances remain very similar (2.000−2.057 Å). Likewise, the lithium−carbon distances in D_2 symmetry[71] Li_2C_4-*t*-Bu_4 are 2.012 to 2.038 Å. Thus, lithium complexation appears to enhance the aromatic effects of the four-membered ring by reducing electron repulsion. The aromatic properties of $Li_2C_4R_4$ are revealed by the NICS(0) (Table 1, −22 to −24 ppm) values which are more negative (aromatic) than benzene and by the ^{7}Li chemical shifts which vary from −2.3 to −3.4 ppm with respect to Li^+. For comparison, the ^{7}Li chemical shift (ppm) of other aromatic Li complexes are Li−benzene$^+$ (−7.3, GIAO-MP2;[72] −6.6 GIAO[63f]), Li−cyclopentadiene (−6.9, GIAO;[73] −8.4, exptl[73]), and Li_2−biphenylene (−7.0, exptl[32]).

Conclusions

The steric bulk of the *tert*-butyl groups in cyclobutadiene and tetrahedrane decreases the symmetries from that of the parent molecules. The standard heat of formation (298 K) of tetra-*tert*-butylcyclobutadiene is calculated from isodesmic reactions to be 33.3 kcal/mol, which is slightly greater than that of tetra-*tert*-butyltetrahedrane (31.9 kcal/mol). The *tert*-butyl-substituted cyclobutadiene dianion and dication are 115.1 and 355.7 kcal/mol higher in energy than the neutral form. (However, the dianion is not bound toward electron loss at the levels employed for this estimation.)

When solvation effects are estimated in acetonitrile, the values become −39.7 and 196.2 kcal/mol, respectively. The presence of Li^+ or other counterions will stabilize the dianion further. Substituent effects on automerization were predicted in C_4R_3H, R = H, Me, and *t*-Bu, based on open-shell singlet calculations of the biradical transition state.

Nucleus-independent chemical shifts (NICS) confirms the antiaromaticity of C_4H_4 and its alkyl derivatives, as well as the aromaticity of the corresponding dications and the dilithium cation-stabilized dianion systems.

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Supporting Information Available: Cartesian coordinates for relevant structures optimized at the B3LYP/6-31G(d) level are given in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(71) At the HF/6-31G(d) level, the D_2 symmetry structure is a transition state to a C_2 symmetry structure which is 0.3 kcal/mol lower in energy. Given the small energy difference, the DFT optimization was not carried out in C_2 symmetry.

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