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Sterically Crowded Bicyclo[1.1.0]butane Radical Cations

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Abstract: The variability of carbon−carbon single bonds by steric and electronic effects is probed by DFT calculations of sterically crowded bicyclo[1.1.0]butanes and their radical cations. The interplay of sterics and electronics on the gradual weakening and breaking of bonds was studied by investigating bridgehead substitution in 1,3-di-*tert*-butylbicyclo[1.1.0]butane and 2,2′,4,4′-tetramethyl-1,3-di-*tert*-butylbicyclo[1.1.0]butane and geminal substitution in 2,2′-di-*tert*-butylbicyclo[1.1.0]butane and 2,2′,4,4′-tetra-*tert*-butylbicyclo[1.1.0]butane. Bridgehead substitution leads to a lengthening of the central bond, whereas bisubstitution on the geminal carbon leads to a shortening of this bond due to a Thorpe−Ingold effect. Although the character of the central bond can be modulated by substitution and electron transfer over a range of 0.35 Å, the state forbidden ring planarization does not occur. Sterically crowded bicyclo[1.1.0]butane radical cations are therefore promising candidates for the investigation of extremely long carbon−carbon single bonds.

The study of the chemical bond is often driven by the investigation of extreme examples. The search for extremely long or extremely short bonds has yielded many interesting structures and important insights into the nature of the chemical bond.[1] One of the most spectacular examples of such studies is the recent isolation of a stable biradical **2**. While in the unsubstituted case, the bicyclobutane-like structure **1a** is more stable and the biradical form is predicted to be a transition structure, the electronic characteristics of heteroatoms and steric repulsion by large substituents in **1b** led to a ring opening to form the stable **2b**.[2] This demonstrates that bond lengths can be modulated in a wide range through an interplay of steric and electronic factors.

The search for unusually long carbon−carbon bonds showed a much lower variability of the carbon−carbon bond length. The elongation of a carbon−carbon single bond by less than 0.1 Å is already considered unusual.[1a] One possibility how longer carbon−carbon single bonds could be achieved is by removal of an electron out of the bond. However, this requires that the HOMO is localized in a carbon−carbon single bond and that the oxidation potential of the hydrocarbon is low enough to make the one-electron oxidation feasible. Bicyclo[1.1.0]butane, **3**, is one of the few cases where these conditions are fulfilled. Their unusual structure, particularly the pyramidalization of the bridgehead carbons to an inverted geometry, can be rationalized in terms of Walsh−Mulliken diagrams[3] and has been the topic a numerous studies.[4,5] Although **3** can be considered as an all-carbon analogue of **2**, it exists in the closed form even when large substituents are present. Several of these compounds were prepared by Hopf and co-workers through photocyclization of highly substituted butadienes.[6−8] None of these sterically crowded bicyclobutanes show an unusually enlongated central carbon−carbon bond, as will be demonstrated below.

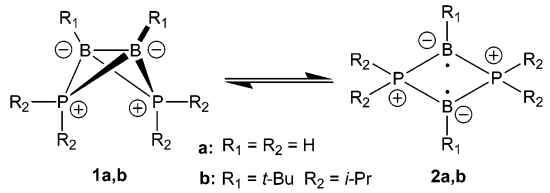

FIGURE 1. Stabilization of singlet diradical by steric repulsion.

The product of the single electron oxidation, bicyclobutane radical cation $\mathbf{3}^{\bullet+}$, has been postulated as an intermediate in the bridging bond bromination[9] and observed by low-temperature ESR.[10] The structure of $\mathbf{3}^{\bullet+}$ has been the subject of an extensive study by Bally.[11] He showed that the ring inversion process through an opened form cyclobutane-1,3-diyl radical cation is state symmetry forbidden within the C_{2v} point group of the $\mathbf{3}^{\bullet+}$ and the system was required to undergo distortion to C_s symmetry in order for the process to occur in an adiabatic fashion. The through-bond interaction of the orbital corresponding to the HOMO of **3**, along with the through-space interaction of the one from the LUMO,[12] leads to a complicated ordering of those orbitals close in energy, as shown in Figure 2.

(1) For some recent examples, compare: Li, P.-C.; Wang, T.-S.; Lee, G.-H.; Liu, Y.-H.; Wang, Y.; Chen, C.-T.; Chao, I. *J. Org. Chem.* **2002**, *67*, 8002. (b) Orimoto, Y.; Aoki, Y. *Intl. J. Quantum Chem.* **2002**, *86*, 456. (c) Tanaka, K.; Takamoto, N.; Tezuka, Y.; Kato, M.; Toda, F. *Tetrahedron* **2001**, *57*, 3761. (d) Toda, F.; Tanaka, K.; Watanabe, M.; Tamura, K.; Miyahara, I.; Nakai, T.; Hirotsu, K. *J. Org. Chem.* **1999**, *64*, 3102.

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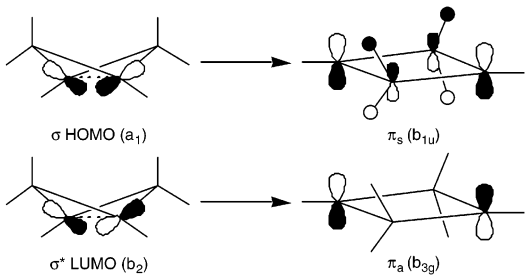

FIGURE 2. Corresponding orbitals in $\mathbf{3}^{\bullet+}$ and its ring opened form.

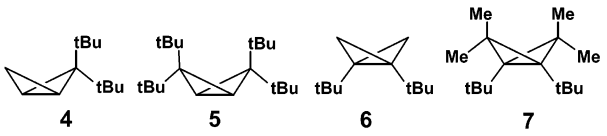

FIGURE 3. Highly substituted [1.1.0] bicyclobutanes.

The sensitivity of the unusual bonding structure of **3** to substituents and to electron transfer (ET) has been established.[11,13] Therefore it is a suitable system to investigate whether the interplay of steric repulsion and electronic factors can lead to a ring opening to form the cyclobutane-1,3-diyl radical cation, in analogy to the heterocyclic derivative **2a**, and to explore the range in which the carbon−carbon single bond length can be modulated. Here, we discuss the effect of bulky substituents at the geminal and bridgehead positions of **3**. To determine the mechanism by which the release of the energy in highly strained molecules is triggered through ET, a series of four substituted bicyclo[1.1.0]butanes **4**−**7**, shown in Figure 3, were studied: geminal substitution effects can be assessed through 2,2′-di-*tert*-butylbicyclo-[1.1.0]butane **4** and 2,2′,4,4′-tetra-*tert*-butylbicyclo[1.1.0]-butane **5**, whereas bridgehead substitution is represented by 1,3-di-*tert*-butylbicyclo[1.1.0]butane **6**. A combination of the two effects will be analyzed for the case of 1,3-di-*tert*-2,2′,4,4′-tetramethyl-butylbicyclo[1.1.0]butane **7**.

Computational Methodology

The accurate treatment of hydrocarbon radical cations remains one of the challenges of modern electronic structure theory.[14a,b] Here, we used the B3LYP hybrid density functional with 6-31G*, which gave results in good agreement with available experimental values for a number of hydrocarbon radical cations.[14b] It was also shown to correctly model steric repulsion between *tert*-butyl groups.[14c,d] We therefore expect that this methodology will be able to adequately describe the systems studied here. All stationary points were characterized by normal-mode analysis. All studies were performed using the G98 series of programs.[15]

The key geometric parameters are designated as shown in Figure 4: **d** and **a** represent the bond lengths of the central and geminal carbon−carbon bonds, respectively. The inversion angle β is defined as the angle between the bridgehead substituent, C_1, and a fictitious point halfway between C_2 and C_4. The puckering angle θ is defined as the angle between C_2, the halfpoint of the central C_1-C_3 bond, and C_4. δ is defined as the angle between that halfpoint, C_2, and the *exo* substituent. δ' is the angle between the *endo* and the *exo* substituents on C_2 and γ is the $C_1-C_2-C_3$ angle. It was shown by Hoz and co-workers that some of the geometric parameters are strongly coupled to each other.[13c]

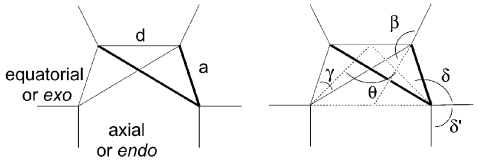

FIGURE 4. Definition of distances and substituents (left) and characteristic angles (right) in **3**.[4a]

TABLE 1. Selected Geometric Parameters of 3 and $\mathbf{3}^{\bullet+}$

	neutral		cation	
	calcd	exptl[a]	calcd	exptl[b]
d (Å)	1.49	1.497	1.70	1.786 ± 0.003
θ (deg)	122.2	121.7	135.3	132 ± 2.5

[a] Microwave spectrum.[16] [b] Derived from ESR spectra using MNDO calculations.[10a]

As a reference for the geometric changes and to validate the methodology used, we began our studies with the reinvestigation of **3** and $\mathbf{3}^{\bullet+}$ at the level of theory used here. The main changes upon ionization of **3** are an increase of the puckering angle θ of 13.1° and an increase in the central bond length, **d**, by 0.2 Å, as summarized in Table 1. The inversion angle β decreases by almost 14° upon ET. This is in agreement with the increase of θ through pyramidalization of the bridgehead carbons as described above. Figure 5 shows three different views of **3**. The inversion angle β is 169.3° and decreases to 155.4° on ionization. This was previously rationalized in terms of a better orbital alignment as the dominant effect. Further flattening of the cycle would eventually increase toward a planarization of the bridgehead centers and breaking of the central bond.

These results are consistent with a weakening of the central bond by electron transfer. Similar to the case of **1a**, this effect is not strong enough to cause a complete disruption of the bond in the absence of steric repulsion.

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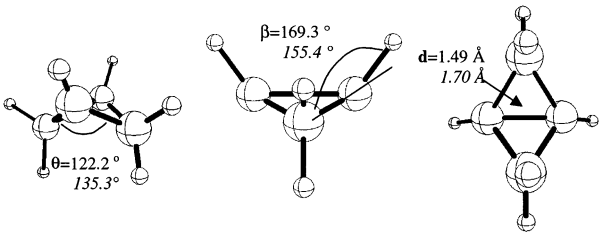

FIGURE 5. Structure of **3**. Selected geometric parameters for the radical cation **3**$^{\bullet+}$ are shown in italics.

TABLE 2. Hyperfine Coupling Constants of 3$^{\bullet+}$

	calcd (mT)	exptl[10a] (mT, ± 0.05)
$H_{equatorial\ (exo)}$	+1.30	+1.14
$H_{axial\ (endo)}$	+7.98	+7.71
$H_{bridgehead}$	−1.09	−1.14

TABLE 3. Selected Geometrical Parameters for 4−7

		3	4	5	6	7
d (Å)	neutral	1.49	1.52	1.54	1.48	1.52
	radical cation	1.70	1.66	1.67	1.76	1.84
a (Å)	neutral	1.50	1.52	1.54	1.51	1.53
	radical cation	1.50	1.49	1.51	1.50	1.52
θ (deg)	neutral	122.2	133.2	145.8	116.8	123.2
	radical cation	135.3	141.7	153.3	132.8	143.4
β (deg)	neutral	169.3	160.0	152.9	173.4	175.6
	radical cation	155.4	153.8	149.7	169.4	171.6
δ (deg)	neutral	121.5	114.8	113.9	121.4	120.5
	radical cation	127.7	119.7	117.4	127.6	126.6
δ' (deg)	neutral	113.8	118.1	113.9	113.7	108.1
	radical cation	113.0	118.7	113.0	112.0	107.1
γ (deg)	neutral	69.4	60.1 (61.0)[a]	60.4	58.9	59.8
	radical cation	69.4	67.9 (68.0)[a]	67.2	71.8	74.8

[a] Value in parentheses is for the unsubstituted carbon in the unsymmetric compound **4**.

This indicates that the system is indeed suitable for the investigation of the interplay of steric and electronic factors, as formulated in the original hypothesis. Furthermore, the computational values for the hyperfine coupling constants derived from the Fermi contacts terms are in excellent agreement with ESR experimental results,[10] as shown in Table 2. This reemphasizes the expectation that the B3LYP/6-31G* method will be able to accurately predict the geometric and electronic structure of bicyclo[1.1.0]butane radical cations. We thus turned to a series of sterically crowded bicyclobutanes. Relevant geometrical parameters of sterically crowded bicyclo[1.1.0]butanes **4**−**7**, reference compound **3** and their corresponding radical cations are presented in Table 3.

Geminal Substitution. The bicyclobutane ring system in **4** and **5** (Figures 6 and 7) is destabilized through geminal bisubstitution. This is due to three different types of steric interactions of the substituents: (i) *endo* substituent at C_2 with the hydrogen or alkyl substituent in the *endo* position at C_4, (ii) geminal substituents at C_2 (Thorpe−Ingold effect), and (iii) *exo* substituents at C_2 with the hydrogens on the bridgehead carbons.

Several interrelated geometric parameters change as a result of these interactions upon going from the unsubstituted **3** to **4** or **5**. First, the puckering angle θ increases by 11° and 23.6° in **4** and **5**, respectively. This

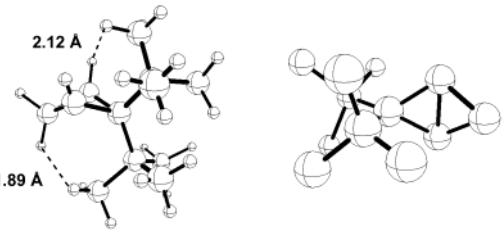

FIGURE 6. B3LYP/6-31G* structure of **4**$^{\bullet+}$. Hydrogen atoms are omitted for clarity on the right.

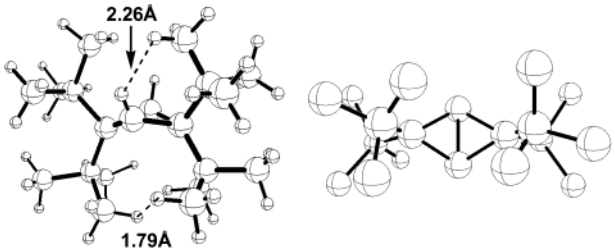

FIGURE 7. B3LYP/6-31G* structure of **5**$^{\bullet+}$. Hydrogen atoms are omitted for clarity on the right.

is due to the repulsion of the *endo* substituents, which come into van der Waals contact, as can be seen from the nonbonded distances of 1.89 and 1.79 Å shown in Figures 6 and 7. It also leads to a small but significant elongation of the central carbon−carbon bond by 0.03 and 0.05 Å in **4** and **5**, respectively. Second, the angle δ' between the geminal substituents increases in **4** as the result of a Thorpe−Ingold effect.[17] In an sp^3-hybridized carbon, the geminal substituents increase the $C_{sub}-C_{sp3}-C_{sub}$ (δ' in BCB) angle as a result of steric repulsion. In turn, the complementary angle between the two other substituents on this carbon (γ in **3**) decreases. The Thorpe−Ingold effect has been shown to play a role in reactivity,[18] and in this case it prevents the bridging bond from extending too far, since planarization would bring the two *tert*-butyl groups in close contact. In the series of neutral compounds, the Thorpe−Ingold effect also contributes to an increase in the puckering angle θ to offset this effect rather than a decrease of **d**. This is because a further compression of the already short central carbon−carbon single bond (**d** = 1.49 Å in **3**) is not feasible since the potential for this bond is much stiffer than the relatively soft potential for the two angles θ and γ. Third, the repulsion of the *endo* substituents and the Thorpe−Ingold effect move the *exo* substituents closer to the bridgehead hydrogen, decreasing the angle δ and leading to nonbonded distances of 2.12 and 2.26 Å in **4** and **5**, respectively. Further compression of δ is not possible because of these close contacts. This is why, in **5**, δ' returns to a value closer to the 114° observed in **3**.

Upon ionization, **d** increases by 0.14 and 0.13 Å, respectively, less than in the unsubstituted case. This is

(17) Control calculations showed that this occurs only in case of geminal bisubstitution, monosubstitution in either the *endo* or *exo* position leads to a distortion of δ and δ' but has little effect on the bicyclobutane system.

(18) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224.

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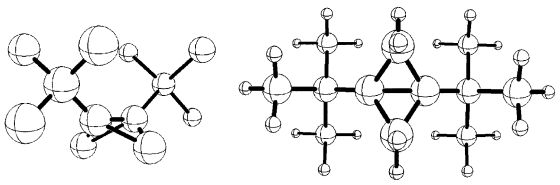

FIGURE 8. B3LYP/6-31G* structure of $\mathbf{6}^{\bullet+}$. Hydrogen atoms are omitted for clarity on the left.

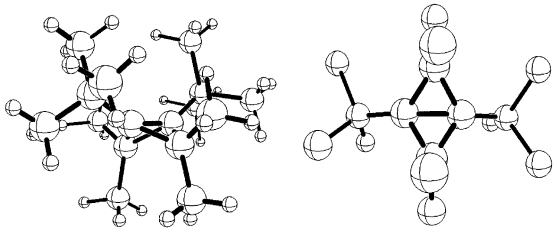

FIGURE 9. B3LYP/6-31G* structure of $\mathbf{7}^{\bullet+}$. Hydrogen atoms are omitted for clarity on the right.

again consistent with a Thorpe−Ingold (or *gem*-dialkyl) effect of the two geminal substituents. In the radical cation series, it makes the effect of ionization on the central bond length and the puckering angle θ smaller in $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ than in $\mathbf{3}^{\bullet+}$. The other geometric parameters are related to the results obtained for **d** and follow the same trends discussed above. These effects are not additive in going from $\mathbf{4}^{\bullet+}$ to $\mathbf{5}^{\bullet+}$, because the opening of the angle δ' between the *tert*-butyl substituents at both geminal positions is hindered through the steric repulsion of the two *endo* substituents at positions 2 and 4. In summary, the overall effect of geminal substitution is opposite for the neutral compounds and the corresponding radical cations. To lengthen the central carbon−carbon bond, smaller geminal substituents have to be used. We therefore investigated the effect of bridgehead substitution on a weakening of the central C−C bond.

Bridgehead Substitution. Substitution at the bridgehead carbons in **6** has only a small effect on the geometric parameters, and neutral **6** closely resembles the parent compound **3**. This indicates that the steric repulsion in neutral **6** is relatively small as compared to the strength of the central carbon−carbon bond. However, ionization to the radical cation $\mathbf{6}^{\bullet+}$, shown in Figure 8, leads to a lengthening of the central carbon−carbon bond by 0.28 Å, more than the unsubstituted case. The *tert*-butyl groups have two effects: a steric effect across the central bond that forces an elongation and a stabilization of both radical and positive centers via hyperconjugation, thus driving the structure toward a localized spin and charge one. This propensity is also reflected in the puckering angle θ, which is increased by 16° to 132.8°.

The interaction of the two *tert*-butyl groups has also an effect on the inversion angle β, which is increased by 4.1° as compared to **3**. Upon ionization, however, only a 4° decrease is observed; the bridgehead substitution compensates for the ionization. The overall effect is close to zero.

The combination of geminal substitution as in **7** (Figure 9) is a combination of the effects observed earlier. The central bond **d** and the puckering angle θ present the greatest increase upon ionization. Nevertheless, the central carbon−carbon bond is with a bond length of 1.84 Å still existent, indicating that electron transfer and steric repulsion are sufficient to modulate the bond length by 0.32 Å but not to completely break the bond. This increase in bond length is accompanied by an increase in the puckering angle by 20.2°. The *endo* interaction is stronger than a weaker Thorpe−Ingold effect of the geminal methyl groups, which cannot be strong enough to compensate for the ionization and the steric repulsion of the bridgehead substituents. The inversion angle is also affected; a 4° decrease in the radical cation, combined with a 6.3° increase compared with the neutral **3**, creates a +2.3° effect. This is due to the interaction of the *exo* methyl group, which interacts with the two bridgehead *tert*-butyl groups.

The effects of bridgehead and geminal substitution effects on the structure of bicyclo[1.1.0]butane neutral and radical cation were studied. Whereas the effect of steric repulsion in the neutral derivatives is with a maximum elongation of the central carbon−carbon bond of 0.05 Å relatively small, much larger effects are obtained for the corresponding radical cations. Upon removal of an electron from the central carbon−carbon single bond, the length of this bond increases between 0.13 and 0.32 Å. The weakened one-electron bond is much more susceptible to steric effects, leading to a variability of the bond lengths of 0.18 Å between the different derivatives. Other geometrical distortions are observed and can be rationalized in terms of steric repulsion of the *tert*-butyl groups and consecutive inward movements of the bridgehead substituents. The larger effect of the bridgehead substitution is in agreement with previous studies of the oxidation of strained organic compounds. On the basis of experimental evidenceand molecular orbital calculations,[20] the effect of bridgehead substitution was again found to be larger than that of geminal substitution. Although substitution has a strong effect on the geometry of the bicyclobutanes considered, steric effects are not sufficient to overcome the electronic effects of a delocalized bond in the radical cation species. This is in contrast to recent findings on an isoelectronic heteroanalogue, where ring opening and formation of a stable biradical could be forced through steric repulsion, emphasizing the importance of state correlations for open shell species. This and the well-known stability of $\mathbf{3}^{\bullet+}$ under ESR conditions[10] make experimental studies of the unusually long carbon−carbon bonds of ∼1.85 Å in the case of $\mathbf{7}^{\bullet+}$ promising. Such studies are currently performed in our laboratory and will be reported in a separate publication.

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Supporting Information Available: Energies, zero point energies, and Cartesian coordinates of all structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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