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Substituent Effects. 2. *n*-Butyl and *tert*-Butyl Derivatives

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The effect of substituent in *n*-butyl and *tert*-butyl derivatives (X = H, CH_3, OH, F, Li, O^-, and NH_3^+) was studied via ab initio mo theory using 6-31G* optimized structures and correction for electron correlation (MP3/6-31G**). The *tert*-butyl/*n*-butyl energy differences were found to depend on the substituent, with electronegative groups preferring *tert*-butyl and the electropositive group, Li, favoring *n*-butyl. Further information was gained by the analysis of bond and atom properties derived from the charge distribution. Most of the bonds in these molecules were found to be bent. The atomic charges at the substituted carbons in the two series were found to be linearly related with a slope of 0.91. The atom energies for the substituted carbons also were linearly related. The origin of the *n*-butyl/*tert*-butyl energy differences is discussed.

Introduction

We recently reported a detailed examination of substituent effects in methyl derivatives.[1,2] In a continuation of this study, we have now examined the effects of some substituents on *n*-butyl and *tert*-butyl derivatives. The former will allow an examination of the transmission of substituent effects along an alkyl chain, and the latter will show whether substituents affect a tertiary center in a different way than primary centers. The substituents were chosen to cover a wide range of possible interactions and include CH_3, OH, F, Li, O^-, and NH_3^+.

The structures were optimized at the 6-31G* level, and the corresponding energies are given in Table I. For the subsequent analysis, we wished to have wave functions derived from a better balanced basis set, and therefore 6-31G** calculations were performed using the 6-31G* geometries. It is known that the addition of polarization functions at hydrogens does not have a significant effect on the calculated geometries.[3]

We were interested in examining the effect of substituents on the difference in energy between *n*-butyl and *tert*-butyl compounds. Since the relative energies appear to be affected by correction for electron correlation, the MP2 and MP3 corrections to the RHF/6-31G** energies also were obtained and are given in Table I. The energy differences are summarized in Table II. The difference is known for two cases, *n*-butane vs isobutane, and *n*-pentane vs neopentane.[4] The experimental values, corrected to 0 K and for the difference in zero-point energies also are given. The MP2 energies overcorrect as is often observed,[5] and the MP3 energies would be expected to be close to the correct answer. The agreement for the two known cases appears to be quite satisfactory. We shall assume that the other energy changes are equally satisfactory.

Table I. Energies (H) of *n*-Butyl and *tert*-Butyl Derivatives

compound	6-31G* RHF	6-31G**//6-31G* RHF	MP2	MP3
n-butane	−157.29841	−157.31395	−157.90728	−157.95783
isobutane	−157.29898	−157.31456	−157.90985	−157.95980
n-butyllithium	−164.11235	−164.12663	−164.72741	−164.77363
tert-butyllithium	−164.10278	−164.11658	−164.72261	−164.76710
n-butyl fluoride	−256.14684	−256.16107	−256.91192	−256.95734
tert-butyl fluoride	−256.15900	−256.17339	−256.92896	−256.97294
n-butyl alcohol	−232.14509	−232.16554	−232.93164	−232.98120
tert-butyl alcohol	−232.15335	−232.17405	−232.94615	−232.99398
n-butoxide ion	−321.50107	−231.51532	−232.28823	−232.33140
tert-butoxide ion	−231.51319	−231.52727	−232.30567	−232.34706
n-butylammonium ion	−212.68917	−212.71349	−213.47216	−213.53008
tert-butylammonium ion	−212.69889	−212.72345	−213.48766	−213.54395
n-pentane	−196.33310	−196.35168	−197.08929	−197.15037
neopentane	−196.33382	−196.35246	−197.09635	−197.15542

Table II. Energy Differences (kcal/mol)

compounds	6-31G* RHF	6-31G**//6-31G** RHF	MP2	MP3	expt
isobutane–butane	−0.36	−0.38	−1.61	−1.24	−1.5 ± 0.2
t-BuLi–BuLi	+6.01	+6.31	+3.01	+4.10	
t-BuF–BuF	−7.63	−7.73	−10.7	−9.79	
t-BuOH–BuOH	−5.18	−5.34	−9.11	−8.02	
t-BuO^-–BuO^-	−7.61	−7.50	−10.94	−9.83	
t-$BuNH_3^+$–$BuNH_3^+$	−6.10	−6.25	−9.73	−8.70	
neopentane–pentane	−0.45	−0.50	−4.43	−3.17	−3.6 ± 0.2

The *tert*-butyl compounds are the more stable in all cases except for the lithio compounds, where *n*-butyllithium is predicted to be kcal/mol more stable than *tert*-butyllithium. This is in accord with the general observation that *tert*-butyllithium is more reactive than *n*-butyllithium,[6] although the difference in aggregation is probably another important factor. Electronegative substituents increase the difference in energy in favor of the *tert*-butyl compound. Thus, it appears that relative to *n*-butyl, electropositive substituents destabilize *tert*-butyl derivatives and electronegative substituents stabilize them. One might have expected the O^- group to act as an electropositive substituent, but as will be shown below, it induces a positive charge at the carbon to which it is atta-

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[1] Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.*, in press.

[2] For recent reviews of the extensive literature on substituent effects, see: Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* 1987, *16*, 1. Topsom, R. D. *Ibid.* 1987, *16*, 85, 125. Charton, M. *Ibid.* 1987, *16*, 287.

[3] In a series of compounds we have examined, going from 6-31G* to 6-31G** led to changes in C–C and C–H bond lengths of less than 0.001 Å.

[4] The enthalpies of formation at 298 K were taken from Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986. The vibrational frequencies were taken from Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Organic Molecules*, Halsted Press: New York, 1974.

[5] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 278ff.

[6] Eisch, J. J. *The Chemistry of Organometallic Compounds*; Macmillan: New York, 1967; p 82.

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ched. Thus, it behaves in a fashion similar to the electronegative substituents.

The reason for the difference in the energy changes between electronegative and electropositive substituents is not obvious, and therefore we have sought further information via an analysis of the wave functions. We have made use of Bader's theory of atoms in molecules[7] to partition the molecule into atomic domains, and then the electron populations and kinetic energies were obtained by numerical integration of the charge density and the kinetic energy, respectively. The bond properties and the structural parameters are given in Table III.

Bond Properties

Bonds are best defined in terms of bond paths which are the paths of maximum charge density between a pair of bonded atoms. Bond angles are then defined as the angle between a pair of bond paths at a given atom. As we have previously noted,[1,8] most bonds are bent. Table III includes a comparison of the bond angles as determined by the bond paths and the conventional bond angles. The largest deviations from the conventional angles were found with the C–O–H bonds of *n*-butyl (7.5°) and *tert*-butyl (8.4°) alcohols. This corresponds to the tendency in water to place the lone pairs in orbitals having high s character.[9] The resulting small C–O–H bond path angle leads to a C···H repulsive interaction and a conventional angle larger than the bond path angle. Large angular deviations also were found with the C–C–N angles of *n*-butylammonium (4.4°) and *tert*-butylammonium (3.7°) ions. Here, the strongly electronegative group prefers high p character in the orbital from carbon[10] and places more s character in the C–C bond. This results in smaller bond path angles which are opposed by the steric interaction between C and N.

Another important quantity is the bond critical point which is the point of minimum charge density along a bond path. The ratios of the distances to the bond critical points ($R = r_A/r_B$ in Table III) are indicators of relative electronegativity.[11] The values of R change in the expected fashion, with the C–F bond in *n*-butyl fluoride having $R = 0.462$ whereas the C–Li bond in *n*-butyllithium has $R = 1.864$.

Atom Properties

The electron populations and atom kinetic energies were obtained by numerical integration of the charge density within well-defined atomic volumes.[7] These volumes were derived by starting at the bond critical points and developing rays for which the charge density decreases most rapidly. The set of such rays form a surface which separates a given pair of atoms. The set of surfaces about a given atom serves to define its volume. The results are given in Table IV. Here, n is the population for the atom or group, L is the integral of $-(\hbar^2/4m)\nabla^2\rho$ which should be zero for an exact integration, and T is the atom (or group) kinetic energy corrected for the small virial defect found in the SCF calculation. The sum of the populations agree well with the expected values, and the sum of the atom kinetic energies agree well with the negative of the total energy obtained in the SCF calculation, as required by the virial theorem.

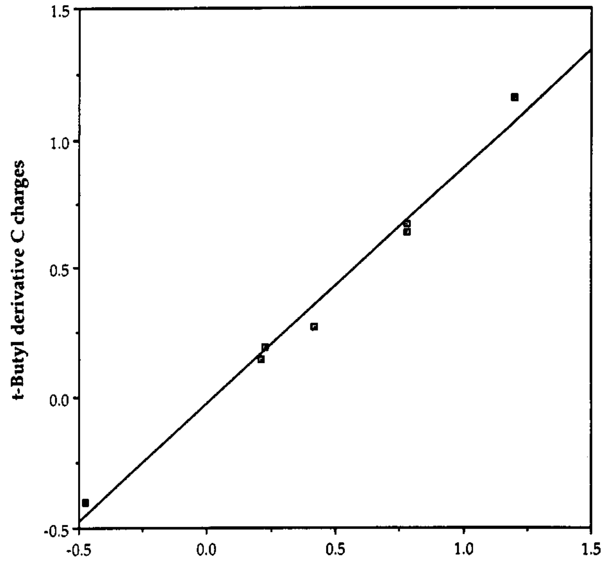

Figure 1. Correlation between the atomic charges for the substituted carbons of *tert*-butyl and *n*-butyl derivatives.

We were particularly interested in the relationship between the *n*-butyl and *tert*-butyl derivatives. The electron populations have been converted to the equivalent charges by subtracting the population from the nuclear charge, and are summarized in Table V. One might first note the small changes in charge at the terminal methyl and methylene carbons of the *n*-butyl derivatives. A somewhat greater effect is seen at C2, but the major changes are found at C1. With the exception of *tert*-butoxide ion, the charges at the methyl carbons of the *tert*-butyl derivatives are again little affected by the substituents.

Larger changes are found with the methyl and methylene groups, and this results from the changes in hydrogen charges. For example, at the terminal methyl group of *n*-butane, the hydrogen charges at −0.079 (in the plane of the carbon atoms) and −0.082. For the *n*-butyl derivatives, the hydrogen charges at the terminal methyl become −0.034 and −0.060 with the NH_3^+ substituent and −0.125 and −0.103 with the O^- substituent. Thus, even at a long distance from the substituent, the hydrogen charges are significantly affected. The small change in carbon charges and the larger change in hydrogen charges suggests that except at the site of substitution, the carbons tend to maintain their atomic volumes and electron populations, and the remote substituent effects manifest themselves in changes in the hydrogen populations which result largely from the shift in the C–H dividing surface and the consequent change in volume associated with the hydrogens.[1]

The charges at the substituted carbons cover a wide range. A difference in electronegativity between atoms forming a bond will result in a charge shift toward the more electronegative atom, and a shift in the bond critical point (and the dividing surface) away from the more electronegative atom.[1] This atom will gain electron population in two ways, from the shift in charge density and from the increase in volume associated with the atom. The relative importance of these terms has been evaluated for a series of methyl derivatives.[1] It is important to note that the atoms defined by the theory of atoms in molecules are not spherical and that the center of electron charge generally

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Table III. Calculated Structures and Bond Properties of *n*-Butyl and *tert*-Butyl Derivatives[a]

compound	parameter	value	$r_{\mathrm{A}}/r_{\mathrm{B}}$ or bp angle	ρ_c	$\nabla^2\rho$	ϵ
n-butane	*r*(C1C2)	1.5280	1.011	0.2545	−0.6720	0.0066
	r(C2C3)	1.5297	1.000	0.2561	−0.6774	0.0159
	r(C1Ha)	1.0857	1.543	0.2864	−1.0546	0.0071
	r(C1Hb)	1.0865	1.540	0.2858	−1.0490	0.0064
	r(C2H)	1.0881	1.528	0.2870	−1.0528	0.0054
	C1C2C3	113.08	111.86			
	C2C1Ha	111.30	110.83			
	C2C1Hb	111.15	109.95			
	C1C2H	109.40	109.39			
n-butyllithium	*r*(C3C4)	1.5299	0.958	0.2534	−0.6670	0.0038
	r(C2C3)	1.5351	0.955	0.2543	−0.6689	0.0173
	r(C1C2)	1.5386	0.916	0.2447	−0.6109	0.0617
	r(CLi)	2.0195	1.864	0.0413	0.2026	0.0133
	r(C4Ha)	1.0869	1.526	0.2847	−1.0404	0.0041
	r(C4Hb)	1.0873	1.526	0.2846	−1.0381	0.0034
	r(C3H)	1.0885	1.517	0.2860	−1.0449	0.0099
	r(C2H)	1.0924	1.479	0.2822	−1.0147	0.0098
	r(C1H)	1.0964	1.442	0.2690	−0.8972	0.0861
	C2C3C4	113.66	112.26			
	C1C2C3	115.21	113.67			
	C2C1Li	117.84	115.92			
	C3C4Ha	111.69	111.16			
	C3C4Hb	111.15	110.28			
	C4C3H	109.43	109.01			
	C3C2H	107.84	107.07			
	C2C1H	108.29	105.71			
n-butyl fluoride	*r*(C3C4)	1.5280	1.005	0.2452	−0.6702	0.0071
	r(C2C3)	1.5297	1.013	0.2546	−0.6699	0.0099
	r(C1C2)	1.5148	1.078	0.2699	−0.7617	0.0538
	r(C1F)	1.3728	0.462	0.2311	0.4871	0.0062
	r(C4Ha)	1.0852	1.550	0.2871	−1.0611	0.0086
	r(C4Hb)	1.0860	1.548	0.2865	−1.0550	0.0079
	r(C3H)	1.0880	1.533	0.2873	−1.0551	0.0047
	r(C2H)	1.0866	1.533	0.2885	−1.0656	0.0019
	r(C1H)	1.0834	1.619	0.3022	−1.1942	0.0596
	C2C3C4	112.69	111.44			
	C1C2C3	112.55	111.90			
	C2C1F	109.54	107.30			
	C3C4Ha	111.13	110.63			
	C3C4Hb	111.11	109.77			
	C4C3H	109.26	109.45			
	C3C2H	110.15	109.77			
	C2C1F	111.51	112.87			
n-butyl alcohol	*r*(C3C4)	1.5283	0.997	0.2542	−0.6701	0.0068
	r(C2C3)	1.5294	1.002	0.2554	−0.6738	0.0122
	r(C1C2)	1.5184	1.059	0.2666	−0.7430	0.0480
	r(CO)	1.4041	0.466	0.2609	−1.4732	0.0056
	r(C4Ha)	1.0855	1.544	0.2867	−1.0571	0.0080
	r(C4Hb)	1.0861	1.545	0.2863	−1.0532	0.0072
	r(C3H)	1.0882	1.528	0.2869	−1.0526	0.0041
	r(C2H)	1.0867	1.552	0.2884	−1.0652	0.0032
	r(C1H)	1.0893	1.562	0.2942	−1.1189	0.0497
	r(OH)	0.9465	4.136	0.3901	−0.2399	0.0283
	C2C3C4	112.73	111.61			
	C1C2C3	112.98	112.18			
	C2C1O	108.22	108.64			
	C3C4Ha	111.22	110.71			
	C3C4Hb	111.10	109.85			
	C4C3H	109.35	109.30			
	C3C2H	110.11	109.69			
	C2C1H	109.99	111.31			
	C1OH	109.67	102.17			
n-butoxide ion	*r*(C3C4)	1.5311	0.924	0.2509	−0.6627	0.0013
	r(C2C3)	1.5302	0.897	0.2535	−0.6707	0.0043
	r(C1C2)	1.5578	0.853	0.2440	−0.6446	0.0487
	r(CO)	1.3122	0.494	0.3486	−0.7041	0.0086
	r(C4Ha)	1.0901	1.488	0.2812	−1.0115	0.023
	r(C4Hb)	1.0878	1.517	0.2839	−1.0332	0.0033
	r(C3H)	1.0899	1.500	0.2841	−1.0287	0.0129
	r(C2H)	1.0909	1.482	0.2815	−1.0082	0.0270
	r(C1H)	1.1311	1.420	0.2590	−0.8544	0.028
	C2C3C4	114.10	112.66			
	C1C2C3	115.58	114.28			
	C2C1O	113.74	115.61			
	C3C4Ha	112.17	111.42			
	C3C4Hb	111.00	110.54			
	C4C3H	108.86	107.74			
	C3C2H	109.74	107.80			
	C2C1H	104.28	102.17			
n-butylammonium ion	*r*(C3C4)	1.5280	1.063	0.2536	−0.6691	0.0077
	r(C2C3)	1.5343	1.119	0.2505	−0.6576	0.0125
	r(C1C2)	1.5221	1.193	0.2589	−0.7157	0.0218
	r(CN)	1.5192	0.465	0.2135	−0.2115	0.0005
	r(C4Ha)	1.0831	1.603	0.2903	−1.0925	0.0119
	r(C4Hb)	1.0851	1.568	0.2879	−1.0679	0.0139
	r(C3H)	1.0864	1.567	0.2900	−1.0797	0.0129
	r(C2H)	1.0874	1.574	0.2891	−1.0730	0.0176
	r(C1H)	1.0803	1.710	0.3028	−1.2115	0.0458
	r(NHa)	1.0113	3.488	0.3535	−2.0405	0.0007
	r(NHb)	1.0111	3.482	0.3539	−2.0442	0.0010
	C2C3C4	112.04	110.34			
	C1C2C3	111.23	110.64			
	C2C1N	110.37	105.98			
	C3C4Ha	110.37	109.98			
	C3C4Hb	111.30	109.28			
	C4C3H	109.61	110.77			
	C3C2H	109.51	110.79			
	C1NHa	112.03	111.56			
	C1NHb	111.28	110.53			
n-pentane	*r*(C1C2)	1.5269	1.011	0.2543	−0.6710	0.0066
	r(C2C3)	1.5281	1.000	0.2559	−0.6768	0.0143
	r(C1Ha)	1.0848	1.543	0.2864	−1.0549	0.0073
	r(C1Hb)	1.0863	1.540	0.2859	−1.0494	0.0065
	r(C2H)	1.0885	1.528	0.2871	−1.0531	0.0053
	r(C3H)	1.0895	1.524	0.2860	−1.0443	0.0037
	C1C2C3	113.05	111.81			
	C2C1Ha	111.30	110.83			
	C2C1Hb	111.14	109.94			
	C1C2H	109.29	109.10			
	C2C3H	109.25	108.95			
isobutane	*r*(C1C2)	1.5302	1.018	0.2552	−0.6738	0.0071
	r(C1Ha)	1.0874	1.538	0.2850	−1.0418	0.0048
	r(C1Hb)	1.0861	1.540	0.2861	−1.0513	0.0059
	r(C2H)	1.0884	1.524	0.2889	−1.0637	0.0000
	C1C2C3	111.04	110.20			
	C2C1Ha	110.89	109.44			
	C2C1Hb	111.27	110.47			
	C2C1H	107.85	108.73			
tert-butyllithium	*r*(C1C2)	1.5367	1.119	0.2476	−0.6254	0.0806
	r(C1Ha)	1.0980	1.514	0.2771	−0.9777	0.0005
	r(C1Hb)	1.0904	1.486	0.2812	−1.0122	0.0058
	r(CLi)	2.0522	1.896	0.0400	0.1964	0.000
	C2C1Ha	112.21	109.95			
	C2C1Hb	112.19	112.23			
	C1C2Li	111.05	113.23			
tert-butyl fluoride	*r*(C1C2)	1.5208	0.955	0.2684	−0.7512	0.0423
	r(C1Ha)	1.0850	1.545	0.2863	−1.0547	0.0056
	r(C1Hb)	1.0843	1.566	0.2881	−1.0688	0.0045
	r(CF)	1.3901	0.461	0.2215	0.4390	0.000
	C2C1Ha	110.87	110.08			
	C2C1Hb	110.30	108.98			
	C1C2F	106.62	104.86			
tert-butyl alcohol	*r*(C1C2)	1.5226	0.962	0.2656	−0.7369	0.0354
	r(C1Ha)	1.0853	1.535	0.2862	−1.0522	0.0070
	r(C1Hb)	1.0842	1.566	0.2882	−1.0695	0.0043
	r(C2C3)	1.5312	0.998	0.2620	−0.7139	0.0373
	r(C3Ha)	1.0854	1.543	0.2862	−1.0531	0.0039
	r(C3Hb)	1.0872	1.524	0.2844	−1.0358	0.0373
	r(C3Hc)	1.0849	1.564	0.2877	−1.0655	0.0029
	r(CO)	1.4155	0.466	0.2552	−0.1635	0.0008
	r(OH)	0.9477	4.115	0.3883	−2.3754	0.0280
	C1C2O	105.77	106.65			
	C3C2O	109.33	107.05			
	C2C1Ha	110.99	110.00			
	C2C1Hb	110.22	109.04			
	C2C3Ha	111.45	110.67			
	C2C3Hb	110.61	109.03			
	C2C3Hc	110.45	109.45			
	C2OH	109.44	101.00			
tert-butoxide ion	*r*(CC)	1.5813	1.155	0.2439	−0.6389	0.0286
	r(C1Ha)	1.0947	1.438	0.2751	−0.9653	0.0101
	r(C1Hb)	1.0885	1.493	0.2816	−1.015	0.0171
	r(CO)	1.3219	0.496	0.3450	−0.7628	0.0000
	C2C1Ha	114.80	112.09			
	C2C1Hb	108.94	109.68			
	C1C2O	111.67	113.69			

Table III (Continued)

compound	parameter	value	r_A/r_B or bp angle	ρ_c	$\nabla^2\rho$	ϵ
tert-butylammonium ion	r(CC)	1.5257	0.888	0.2610	−0.7129	0.0171
	r(C1Ha)	1.0825	1.650	0.2912	−1.1070	0.0117
	r(C1Hb)	1.0851	1.593	0.2886	−1.0756	0.0181
	r(CN)	1.5440	0.471	0.2022	−0.2217	0.000
	r(NH)	1.0108	3.460	0.3540	2.0372	0.0024
	C2C1Ha	109.06	108.83			
tert-butylammonium ion	C2C1Hb	111.77	108.96			
	C1C2N	106.37	103.20			
	C2NH	111.51	110.80			
neopentane	r(CC)	1.5332	1.021	0.2547	−0.6699	0.0000
	r(C1H)	1.0866	1.538	0.2858	−1.0481	0.0052
	C2C1H	111.15	110.03			

[a] Bond lengths are given in angstroms and bond angles in degrees. The second numerical column gives for the bonds the ratio (*R*) of the distances from the atoms to the bond critical point, and for the angles, the bond path angle. The value of ρ_c is the charge density at the bond critical point (e/au^3), $\nabla^2\rho$ is the sum of the three principal curvatures of ρ at the critical point, and ϵ is the ellipticity (= $\lambda1/\lambda2 - 1$ where the λ's are the negative curvatures of ρ at the critical point).

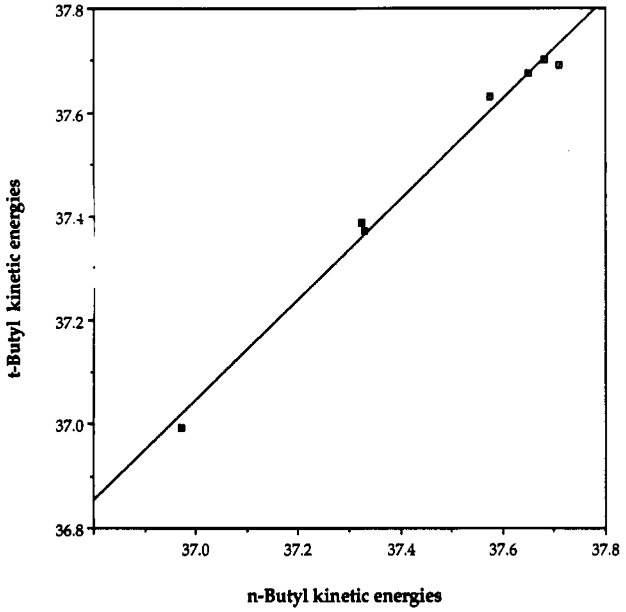

Figure 2. Correlation between the atom kinetic energies for the substituted carbons of *tert*-butyl and *n*-butyl derivatives.

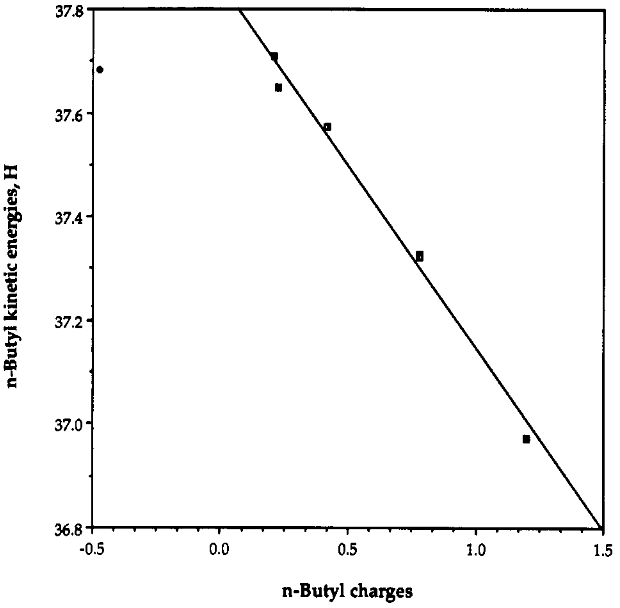

Figure 3. Correlation between the atom kinetic energies for the substituted carbons of *n*-butyl derivatives and the corresponding atomic charges. The point that falls off the line is for *n*-butyllithium.

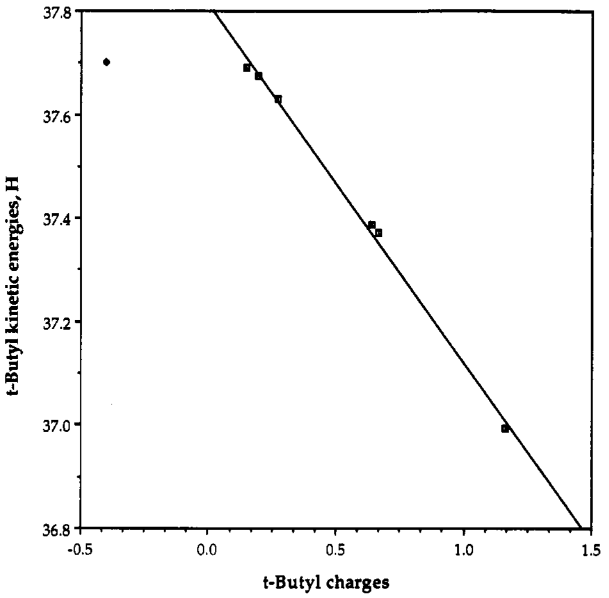

Figure 4. Correlation between the atom kinetic energies for the substituted carbons of *tert*-butyl derivatives and the corresponding atomic charges. The point that falls off the line is for *tert*-butyllithium.

does not coincide with the nuclear positions.

Figure 1 shows the correlation of the atomic charges at the substituted carbons for the two series. The line has a slope of 0.911 (r^2 = 0.985) showing that the effect of substituents for the two series are quite similar, and that *n*-butyl is affected somewhat more strongly than *tert*-butyl. The atom energies may be more important than the charges in determining properties, and they are compared in Figure 2. Again a good linear relationship was found. Here, the slope is 0.966 (r^2 = 0.990). A substituent affects the energy of the *n*-butyl carbon to a greater extent than that of the *tert*-butyl carbon.

An increase in atomic kinetic energy with increasing population would suggest that the atomic volume remains roughly constant. The relationship between the energy and population is shown in Figures 3 and 4 for *n*-butyl and *tert*-butyl, respectively. In both cases, all but one of the substituents fall close to a straight line (*n*-butyl, slope = 0.803, r^2 = 0.988; *tert*-butyl, slope = 0.689, r^2 = 0.996). The unusual substituent is Li which has a smaller than expected atom kinetic energy. Here, the atomic volume of the carbon must increase proportionately to the increase in population so as to keep the kinetic energy constant. This is in accord with the observation that the C–Li "bond" is quite long (2.02 Å) with the bond critical point near the lithium, leading to a large carbon volume in the direction of the lithium.

It is now possible to return to the question as to why electronegative substitutents prefer the *tert*-butyl group whereas the electropositive lithium prefers the *n*-butyl group. The major effect of the substituent is found at the substituted carbon, and Figure 2 shows that the energy of the *tert*-butyl carbon is less strongly effected by substit-

Table IV. Atom Properties of *n*-Butyl and *tert*-Butyl Derivatives, 6-31G**[a]

compound	atom	n	L	T	group	n	L	T
n-BuH	C1	5.7751	−0.0001	37.6487	CH_3	9.0183	0.0000	39.6351
$-V/T$ = 2.00042962	Ha	1.0788	0.0001	0.6614				
E = 157.3140	Hb	1.0821	0.0001	0.6626				
ΔE = 0.25	C2	5.7902	0.0012	37.6722	CH_2	7.9807	0.0012	39.0221
	H	1.0951	0.0001	0.6750				
	sum					33.9980		157.3144
BuLi	C4	5.7849	−0.0005	37.6454	CH_3	9.0635	0.0000	39.6445
$-V/T$ = 2.00029018	Ha	1.0920	0.0001	0.6660				
E = −164.1266	Hb	1.0934	0.0001	0.6666				
ΔE = 0.06	C3	5.7941	0.0008	37.6937	CH_2	8.0038	0.0012	39.0299
	H	1.1049	0.0001	0.6781				
	C2	5.7780	−0.0001	37.6288	CH_2	8.0514	0.0002	39.0110
	H	1.1368	0.0001	0.6911				
	C1	6.4746	−0.0031	37.6814	CH_2	8.7796	−0.0001	39.0393
	H	1.1526	0.0001	0.6790				
	Li	2.0994	0.0002	7.4020				
	sum					35.9977		164.1267
n-BuF	C4	5.7692	−0.0008	37.6634	CH_3	8.9959	0.0000	39.6454
V/T = 2.0009021	Ha	1.0738	0.0001	0.6600				
E = −256.1611	Hb	1.0767	0.0001	0.6610				
ΔE = 0.20	C3	5.7995	0.0011	37.6901	CH_2	7.9827	0.0016	39.0378
	H	1.092	0.0001	0.6738				
	C2	5.7954	−0.0001	37.7344	CH_2	7.9398	0.0016	39.0654
	H	1.0729	0.0001	0.6653				
	C1	5.2182	−0.0032	37.3233	CH_2	7.3333		38.6667
	H	1.0575	0.0001	0.6717				
	F	9.7474	0.0001	99.7461				
	sum					41.9991		255.1614
n-BuOH	C4	5.7702	0.0001	37.6679	CH_3	9.0065	0.0000	39.6533
$-V/T$ = 2.0010045	Ha	1.0781	0.0001	0.6617				
E = −232.1655	Hb	1.0789	0.0001	0.6619				
ΔE = 0.82	C3	5.8034	−0.0055	37.6918	CH_2	7.9944	−0.0052	39.0428
	H	1.0955	0.0001	0.6755				
	C2	5.7956	−0.0062	37.7276	CH_2	7.9412	−0.0031	39.0608
	H	1.0748	0.0001	0.6667				
	C1	5.2209	−0.0021	37.3281	CH_2	7.4077	0.0020	38.6954
	H	1.0933	0.0001	0.6837				
	O	9.2681	0.0002	75.3603				
	H	0.3877	0.0000	0.3516				
	sum					42.0056		232.1642
BuO^-	C4	5.7826	0.0001	37.6460	CH_3	9.1130	0.0000	39.6652
$-V/T$ = 2.00044082	Ha	1.1246	0.0001	0.6782				
E = −231.5153	Hb	1.1027	0.0001	0.6705				
ΔE = 0.50	C3	5.8051	0.0014	37.6726	CH_2	8.0439	0.0013	39.0394
	H	1.1193	0.0001	0.6833				
	C2	5.8336	−0.0045	37.7277	CH_2	8.0903	−0.0006	39.0991
	H	1.1305	0.0001	0.6856				
	C1	4.7987	0.0023	36.9722	CH_2	7.2724	0.0028	38.4125
	O	9.4772	0.0003	75.2999				
	sum					41.9968		231.5161
$BuNH_3^+$	C4	5.7639	0.0002	37.6653	CH_3	8.9180	0.0000	39.6174
$-V/T$ = 2.0009630	Ha	1.0335	0.0001	0.6435				
E = −212.7135	Hb	1.0601	0.0001	0.6544				
ΔE = 0.88	C3	5.7931	−0.0022	37.6853	CH_2	7.9245	−0.0022	39.0126
	H	1.0657	0.0001	0.6637				
	C2	5.8146	−0.0054	37.7200	CH_2	7.9318	−0.0050	39.0383
	H	1.0587	0.0001	0.6591				
	C1	5.5821	0.0012	37.5734	CH_2	7.5477	0.0014	38.8399
	H	0.9828	0.0001	0.6333				
	N	8.2390	−0.0004	55.0212				
	Ha	0.4794	0.0001	0.3933				
	Hb	0.4823	0.0001	0.3947				
	sum					42.0020		212.7121
BuMe	C1	5.7741	0.0002	37.6481	CH_3	9.0179	0.0000	39.6349
$-V/T$ = 2.00042835	Ha	1.0790	0.0001	0.6615				
E = 197.3517	Hb	1.0822	0.0001	0.6627				
ΔE = 0.13	C2	5.7918	−0.0001	37.6709	CH_2	7.9818	0.0004	39.0210
	H	1.0951	0.0001	0.6751				
	C3	5.8040	−0.0001	37.6892	CH_2	7.9994	0.0004	39.0401
	H	1.0978	0.0001	0.6754				
	sum					41.9988		196.3519
t-BuH	C1	5.7832	−0.0010	37.6639	CH_3	9.0299	0.0001	39.6517
$-V/T$ = 2.0004041	Ha	1.0838	0.0001	0.6624				
E = 157.3146	Hb	1.0818	0.0001	0.6627				
ΔE = 0.50	C2	5.8050	0.0041	37.6756				
	H	1.1016	0.0001	0.6847				
	sum					33.9963		157.3154

Table IV (Continued)

compound	atom	n	L	T	group	n	L	T
t-BuLi	C1	5.7953	−0.0011	37.6423	CH_3	9.1639	0.0002	39.6721
$-V/T = 2.00022562$	Ha	1.1171	0.0001	0.6707				
$E = 164.1166$	Hb	1.1268	0.0001	0.6797				
$\Delta E = 0.56$	C2	6.4030	0.0038	37.6997				
	Li	2.1020	0.0002	7.4015				
	sum					35.9967		164.1175
t-BuF	C1	5.7703	−0.0015	37.7105	CH_3	8.9608	0.0000	39.6770
$-V/T = 2.00086957$	Ha	1.0732	0.0001	0.6587				
$E = -256.1734$	Hb	1.0592	0.0001	0.6539				
$\Delta E = 0.38$	C2	5.3610	0.0020	37.3884				
	F	9.7545	0.0000	99.7546				
	sum					41.9979		256.1740
t-BuOH	C1	5.7640	0.0000	37.7060	CH_3	8.9669	0.0001	39.6785
$-V/T = 2.00097124$	Ha	1.0816	0.0001	0.6628				
$E = -232.1741$	Hb	1.0606	0.0001	0.6548				
$\Delta E = 0.19$	C3	5.7860	0.0022	37.7192	CH_3	9.0186	−0.0002	39.7001
	Ha	1.0770	0.0001	0.6606				
	Hb	1.0901	0.0001	0.6659				
	Hc	1.0630	0.0001	0.6552				
	C	5.3320	0.0003	37.3716				
	O	9.2699	0.0003	75.3705				
	H	0.3929	0.0001	0.3530				
	sum					41.9989		232.1738
t-BuO$^-$	C1	5.8201	−0.0024	37.6989	CH_3	9.2278	0.0002	39.7435
$-V/T = 2.00038607$	Ha	1.1678	0.0001	0.6917				
$E = -231.5273$	Hb	1.1212	0.0001	0.6763				
$\Delta E = 0.50$	C2	4.8386	0.0007	36.9944				
	O	9.4770	−0.0012	75.3016				
	sum					41.9990		231.5265
t-BuNH$_3^+$	Cl	5.7861	−0.0020	37.7068	CH_3	8.8568	0.0001	39.6231
$-V/T = 1.0008733$	Ha	0.9960	0.0001	0.6265				
$E = -212.7235$	Hb	1.0381	0.0001	0.6447				
$\Delta E = 0.31$	C2	5.7282	0.0021	37.6312				
	N	8.2297	0.0000	55.0295				
	H	0.4899	0.0001	0.3980				
	sum					41.9980		212.7240
t-BuMe	C1	5.7862	0.0001	37.6754	CH_3	9.0369	0.0001	39.6655
$-V/T = 2.0003702$	H	1.0835	0.0001	0.6633				
$E = -196.3525$								
	C2	5.8509	0.0012	37.6908				
$\Delta E = 0.19$	sum					41.9985		196.3528

[a] The value of n is given in electrons, L and T (the atomic kinetic energy) are given in H, $-V/T$ is the virial defect found in the SCF calculation, E is the total energy found in the SCF calculation, and ΔE is the difference between $-E$ and T in kilocalories/mole.

Table V. Comparison of Group and Atom Charges

X	C4	C3	C2	C1	Me	C3H$_2$	C2H$_2$	C1H$_2$
a. n-Butyl Derivatives								
H	+0.225	+0.210	+0.210	+0.225	−0.018	+0.019	+0.019	+0.061
Li	+0.215	+0.206	+0.222	−0.475	−0.064	−0.004	−0.051	−0.780
CH_3	+0.226	+0.208	+0.196	+0.208	−0.018	+0.018	+0.001	+0.018
HO	+0.230	+0.197	+0.204	+0.779	−0.007	+0.006	+0.059	+0.592
F	+0.231	+0.200	+0.205	+0.782	+0.004	+0.017	+0.060	+0.667
O$^-$	+0.217	+0.195	+0.166	+1.201	−0.113	−0.044	−0.090	+0.728
NH_3^+	+0.236	+0.207	+0.185	+0.418	+0.082	+0.075	+0.062	+0.452

X	C1	C2	Me
b. *tert*-Butyl Derivatives			
H	+0.217	+0.195	−0.030
Li	+0.205	−0.403	−0.164
CH_3	+0.214	+0.149	−0.037
HO	+0.236, +0.214	+0.668	+0.003, −0.019
F	+0.230	+0.639	+0.039
O$^-$	+0.180	+1.161	−0.228
NH_3^+	+0.214	+0.272	+0.143

uents than the carbon of the n-butyl compounds. It must be remembered that the atom kinetic energies (shown in Figure 2) are equal to minus the atom total energy. Therefore an increase in kinetic energy corresponds to a decrease in total energy.

An electronegative substituent will increase the total energy of the carbon, and as a result it is energetically favorable to attach it to the *tert*-butyl group since its energy is less affected. On the other hand, a lithium will decrease the total energy of the attached atom or group, and so it should prefer n-butyl since it will lead to the larger energy decrease. The energy changes are of course seen throughout the molecules, and so the above explanation is an oversimplification. However, since the energy changes are largest at the substituted carbons, it seems appropriate to concentrate on them. It might be noted that the substituent charges and energies for the two series are linearly related with a unit slope.

The reason for the difference in response to substituents is probably found in the geometries of the *n*-butyl and *tert*-butyl compounds (Table III). In the *tert*-butyl series, the C–C–X bond angles to the substituents is smaller than for the *n*-butyl series, and this results from the repulsion between the three methyl groups in the former. A smaller C–C–X angle implies greater ρ orbital character in the C–X bond. Since electronegative substituents prefer an orbital with high p character[9] they will prefer to be bonded to a *tert*-butyl group rather than *n*-butyl.

Calculations

The ab initio calculations were carried out using GAUSSIAN-86,[10] and the analysis of the wave functions was carried out using PROAIMS.[11]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation.

The Thermal Isomerization of [2a,11-$^{13}C_2$]Dicyclopenta[*ef,kl*]heptalene (Azupyrene) to Pyrene

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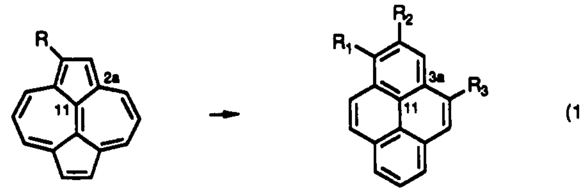
[2a,11-$^{13}C_2$]Dicyclopenta[*ef,kl*]heptalene (azupyrene) has been synthesized from [1,2-$^{13}C_2$]cyclopentanone which, in turn, was prepared from ^{13}C-labeled cyanide and ^{13}C-labeled iodomethane. Thermal isomerization of the labeled azupyrene gave [3a,11-$^{13}C_2$]pyrene. The only proposed mechanisms consistent with this result are the radical-initiated methylene walk and that involving a peripheral bicyclobutane intermediate. These mechanisms are also in agreement with previous results from the isomerization of 1-methylazupyrene except for an additional minor product in the latter experiment. Evidence for the automerization of pyrene under the thermal isomerization conditions has been obtained.

In an earlier study[2] of the thermal isomerization of azupyrene (1) to pyrene (2) the isomerization of 1-methylazupyrene (3) (eq 1) was found to give 1-methylpyrene (4), 2-methylpyrene (5), and 4-methylpyrene (6) in a ratio of 25.5:20.5:5.4. Two of five mechanisms which had been proposed[3] for the thermal isomerization of azulene to naphthalene, the radical-initiated methylene walk (Scheme I) and one initiated by homolysis of a peripheral bridgehead–central carbon bond (Scheme II), were consistent with the formation of approximately equal amounts of 4 and 5. Two other mechanisms, one involving formation of an internal bicyclobutane through symmetry-allowed pericyclic reactions and a stepwise radical process involving a norcaradiene structure, could account for the formation of 6. At that time the desirability of carrying out the isomerization on ^{13}C-labeled azupyrene was noted. The synthesis of [2a,11-$^{13}C_2$]azupyrene (7) and the rearrangement of this to ^{13}C-labeled pyrene are now reported.



(1)

1: R = H

3: R = CH_3

7: R = H; C–2a = C–11 = ^{13}C

2: R_1 = 2_2 = R_3 = H

4: R_1 = CH_3; R_2 = R_3 = H

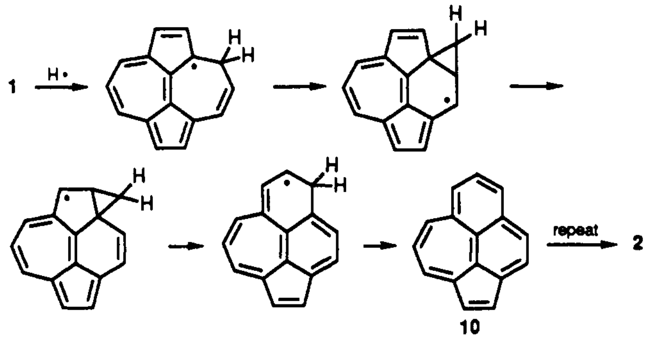
5: R_2 = CH_3; R_1 = R_3 = H

6: R_3 = CH_3; R_1 = R_2 = H

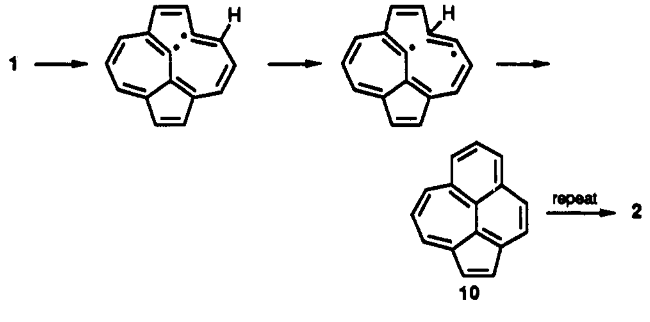
9: R_1 = R_2 = R_3 = H; C–3a = C–11 = ^{13}C

The methylene walk and the bridgehead–central carbon bond homolysis mechanisms differ in that the bond cleavage in the latter leads to the separation in the product of the two carbons whereas in the former these carbons remain at the corresponding positions in the product. As these were the mechanisms of major concern, 7, with adjacent, labeled bridgehead and central carbons, was selected for synthesis.

Scheme I



Scheme II



The incorporation of [1,2-$^{13}C_2$]cyclopentanone (8) in the Jutz synthesis[4] would give 7, and 8 was prepared in 17% overall yield by the route shown (eq 2). The displacement

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(1) From the Ph.D. Thesis of R. D. Haddock, 1989, University of Washington.

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(4) Jutz, C. J.; Schweiger, E. *Synthesis* **1974**, 193.

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