X-ray Studies of Sterically Congested Diphenylethane Derivatives. Substituent Effect on Carbon-Carbon Bond Length

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Crystal structures of several sterically strained diphenylethane derivatives have been obtained. The central C-C bond lengths in these compounds span 1.623 (7) to 1.649 (4) Å but are independent of substitution on the phenyl ring.

An understanding of structural aspects of carbon-carbon bonds can be obtained by investigation of the average situation as well as by exploring the extremes. Unusually long bonds, indicating weakened bonding interactions, are of particular interest.[1,2] To our knowledge, the longest acyclic[3] C-C bond ever reported[4] is 1.67 Å (Scheme I). Even though this bond is only 8% longer than the average (1.54 Å), the number of X-ray structures of compounds with acyclic[3] C-C bonds longer than 1.62 Å is rather limited. Some illustrative examples are shown[5] in Scheme I. Compounds with such strained bonding arrangements provide data for calibration of force field parameters and are of interest from the point of view of structure-reactivity relationships.

Recently, there has been some controversy over the bond length in substituted hexaphenylethanes.[6-8] These sterically crowded molecules are expected to have a significantly elongated central C-C bond. Considerable bond elongation was in fact observed for hexakis(3,5-di-*tert*-butylphenyl)ethane (Scheme I).[6] However, contrary to the results of force field calculations (MM2), hexakis(2,6-di-*tert*-butyl-4-biphenylyl)ethane was observed[8] to have an abnormally short bond of 1.47 (2) Å. Although it has been recently proven by nutation NMR spectroscopy[7] that this result was incorrect, the general question of substituent effect on length of C-C bonds in strained compounds has not been experimentally explored.[9]

This question is especially interesting in systems where the elongated σ-bond can directly overlap with a π-network, electron density of which can be modified by substitution.[2,10,11] The bond elongation should correspond to the lowering of σ* and raising of σ-orbitals of that bond, bringing the energies of these orbitals closer to that of the π-system. This shift in orbital energies may result in a strong interaction between the σ- and π-networks, affecting the bond lengths.[2,10,11] If such interactions were common, the force field parameters would have to be adjusted to give reasonable geometrical data for molecules with appropriately disposed σ- and π-bonds. The hexaphenylethanes discussed above do not provide a fair test for the existence of such interactions due to the propeller shape of the triphenylmethyl moiety. The dihedral angle between the plane of any aromatic ring and the central C-C bond is 45° in these compounds,[6] far from the 90° angle required for maximal overlap.

In connection with our studies of mesolytic cleavage of C-C bonds,[12] we have prepared a series of strained 1,2-diphenyltetraalkylethanes. We report here the single-crystal X-ray data for several of these derivatives and examine the substituent effect on C-C bonds in the 1.62-Å range.

Results and Discussion

The tetraethyl derivatives **1b-d** were prepared by nitration of **1a** followed by appropriate functional group modifications. The tetrabutyl derivatives **2b-c** were obtained by nitration of **2a** or the *m*-fluro derivative of **2a**. The *threo*-**3b** was prepared by nitration of *meso/d,l*-**3a** followed by separation of diastereoisomers. Syntheses[13] of **1a-3a** and crystal structures[13,14] of **1a** and **2a** have been previously reported.

The mononitro derivative, **1b**, was recrystallized from ethanol. The crystals were monoclinic and were assigned to the $P2_1/n$ space group (alternate setting of $P2_1/c$, no. 14) from systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. The dinitro derivative, **1c**, was recrystallized from ethanol. The crystals were monoclinic and belonged to the Cc or $C2/c$ space group based on systematic absences h,k,l, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$. The latter was chosen based on the distribution of E statistics. The nitrodimethylamino derivative, **1c**, was recrystallized from CH_3CN. The crystals were monoclinic and belonged to the $P2_1$ or $P2_1/m$ space group based on systematic absences $0k0$, $k = 2n + 1$. The assignment to the former group was confirmed by successful solution and refinement of the structure with two independent molecules (A and B) in

(1) (a) Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 529. (b) Rüchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem.* **1986**, *130*, 1. (c) Rüchardt, C.; Beckhaus, H.-D *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429.

(2) Osawa, E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, 1986; Vol. 3, p 329.

(3) Only C-C bonds not belonging to any ring structures are discussed here (acyclic bonds). In cyclic bonds there is a possibility for many through-bond and through-space interactions which complicate the analysis. In acyclic compounds the bonds under consideration are the only link between two molecular fragments.

(4) Polishchuk, V. R.; Antipin, M. Y.; Bakhmutov, V. I.; Bubnov, N. N.; Solodovnikov, S. P.; Timofeeva, T. V.; Struchkov, Y. T.; Tumanskii, B. L.; Knunyants, I. L. *Dokl. Acad. Nauk. SSSR* **1979**, *249*, 1125.

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(6) Kahr, B.; Van Engen; D.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 8305 and references therein.

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(8) Stein, M.; Winter, W., Rieker, A. *Angew. Chem. Int., Ed. Engl.* **1978**, *17*, 692.

(9) Compare: Parfonry, A.; Tinant, B.; Declercq, J.-P.; Van Meerssche, M.; Klein, J.; Mernyi, R.; Viehe, H. G. *Bull. Soc. Chim. Belg.* **1987**, *96*, 89.

(10) Dougherty, D. A.; Hounshell, W. D.; Schlegel, H. B.; Bell, R. A.; Mislow, K. *Tetrahedron Lett.* **1976**, *39*, 3479.

(11) Osawa, E.; Ivanov, P. M.; Jaime, C. *J. Org. Chem.* **1983**, *48*, 3990.

(12) (a) Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260. (b) Maslak, P.; Narvaez, J. N. *J. Chem. Soc., Chem. Commun.* **1989**, 138. (c) Maslak, P., Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 283. (d) Maslak, P.; Narvaez, J. N.; Kula, J.; Malinski, D. S. *J. Org. Chem.* **1990**, *55*, 4550. (e) Maslak, P.; Kula, J.; Narvaez, J. N. *J. Org. Chem.* **1990**, *55*, 2277.

(13) Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 3235.

(14) Littke, W.; Drück, U. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 406.

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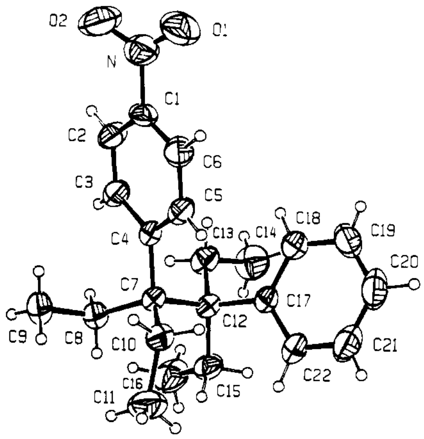


Figure 1. An ORTEP drawing of 3,4-diethyl-3-(4′-nitrophenyl)-4-phenylhexane (**1b**).

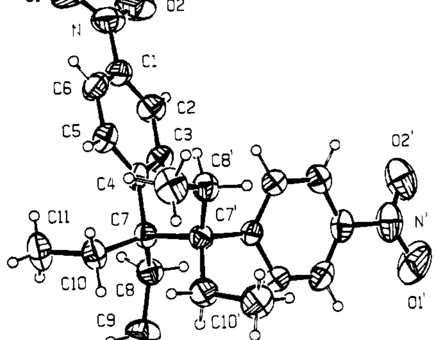


Figure 2. An ORTEP drawing of 3,4-diethyl-3,4-bis(4′-nitrophenyl)hexane (**1c**).

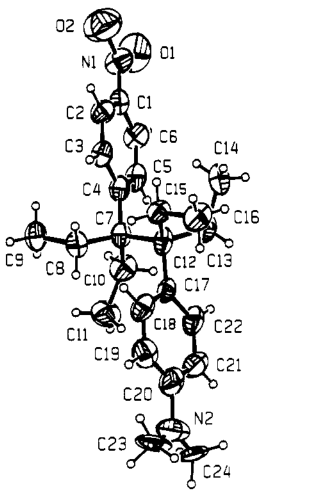


Figure 3. An ORTEP drawing of 3,4-diethyl-3-(4′-nitrophenyl)-4-(4″-(dimethylamino)phenyl)hexane (**1d**, molecule A).

the asymmetric unit (Figure 7).

The mononitro derivatives **2b** and **2c** were recrystallized from ethanol, giving isomorphous monoclinic crystals. The structure was assigned to Cc or $C2/c$ group based on systematic absences. Both structures were successfully refined in the latter space group and showed gross disorder in terms of large thermal motions of the butyl groups, nitro group in **2b**, and nitro as well as fluorine substituents in **2c**.

The mononitro compound, *threo*-**3b** was recrystallized from ethanol. The crystals were orthorombic and belonged uniquely to the $P2_12_12_1$ space group based on systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$ and $00l$, $l = 2n + 1$. The crystal selected for X-ray analysis contained only one enantiomer of **3b**.

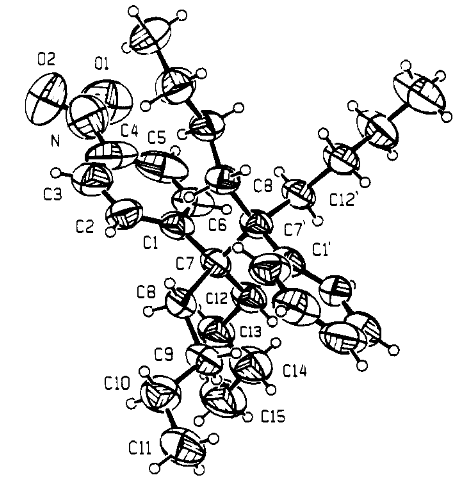


Figure 4. An ORTEP drawing of 5,6-dibutyl-5-(4′-nitrophenyl)-6-phenyldecane (**2b**).

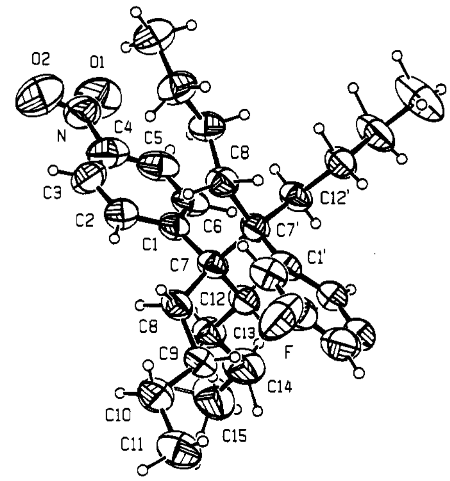


Figure 5. An ORTEP drawing of 5,6-dibutyl-5-(4′-nitrophenyl)-6-(3″-fluorophenyl)decane (**2c**).

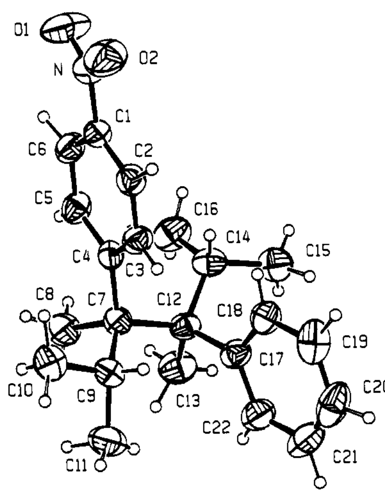


Figure 6. An ORTEP drawing of 2,3,4,5-tetramethyl-3-(4′-nitrophenyl)-4-phenylhexane (**3b**).

The details of X-ray data collection are tabulated in the Experimental Section (Table III). Selected structural data for all the compounds are collected in Tables I and II. Full crystallographic data are presented in the supplementary material. For comparison, the corresponding bond lengths and angles obtained from MM2 calculations[13,15] are also

Scheme I

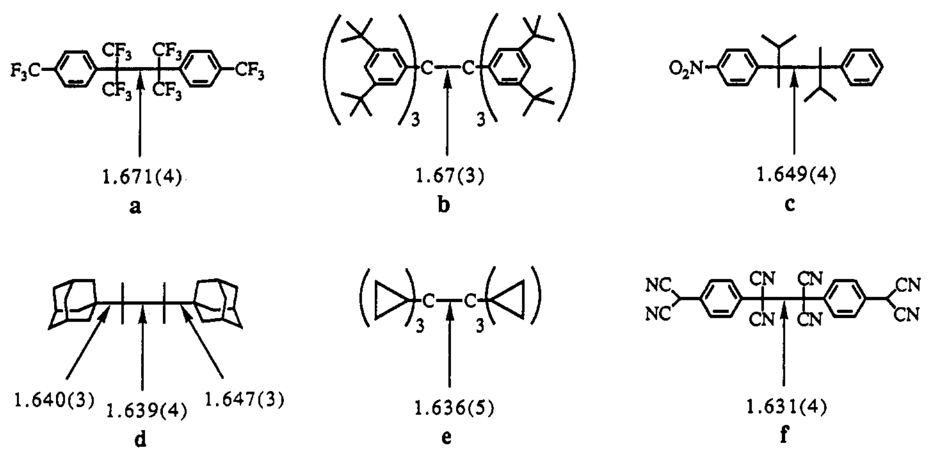
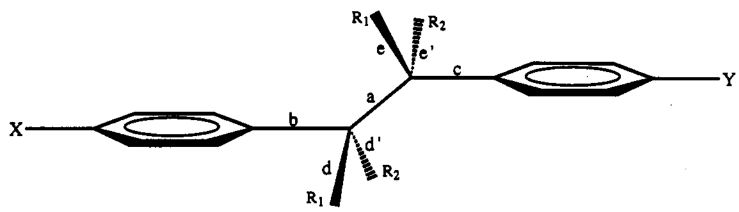


Table I. C–C Bond Lengths (Å) around Quaternary Carbons of Substituted Diphenylethanes[a]



	R_1	R_2	X	Y	*a*	*b*	*c*	*d*(*d*′)	*e*(*e*′)	comm.
1a	Et	Et	H	H	1.621	1.541	1.541	1.568	1.568	MM2[b]
1a	Et	Et	H	H	1.622	1.564	1.553	1.537 1.555	1.536 1.571	C_2[c]
1a	Et	Et	H	H	1.635	1.558	1.558	1.542 1.567	1.542 1.567	C_i[c]
1b	Et	Et	NO_2	H	1.624 (3)	1.542 (3)	1.532 (4)	1.537 (4) 1.549 (4)	1.542 (4) 1.563 (3)	
1c	Et	Et	NO_2	NO_2	1.630 (2)	1.540 (1)	1.540 (1)	1.547 (1) 1.571 (1)	1.547 (1) 1.571 (1)	
1d	Et	Et	NO_2	NMe_2	1.623 (7)	1.534 (6)	1.536 (6)	1.566 (8) 1.579 (8)	1.555 (8) 1.561 (8)	A
1d	Et	Et	NO_2	NMe_2	1.629 (8)	1.535 (6)	1.549 (7)	1.543 (8) 1.559 (8)	1.534 (8) 1.579 (8)	B
2a	Bu	Bu	H	H	1.612	1.546	1.546	1.565 1.573	1.566 1.573	MM2[b]
2a	Bu	Bu	H	H	1.638	1.554	1.554	1.558 1.582	1.558 1.582	*d*
2b	Bu	Bu	NO_2	H	1.636 (6)	1.530 (8)	1.530 (8)	1.546 (6) 1.557 (6)	1.546 (6) 1.557 (6)	
2c	Bu	Bu	NO_2	*m*-F	1.642 (5)	1.520 (5)	1.520 (5)	1.540 (5) 1.579 (5)	1.540 (5) 1.579 (5)	
3a	Me	*i*-Pr	H	H	1.614	1.556	1.556	1.556 1.583	1.556 1.583	MM2[b]
3b	Me	*i*-Pr	NO_2	H	1.649 (4)	1.543 (3)	1.538 (4)	1.548 (3) 1.578 (3)	1.540 (3) 1.581 (4)	

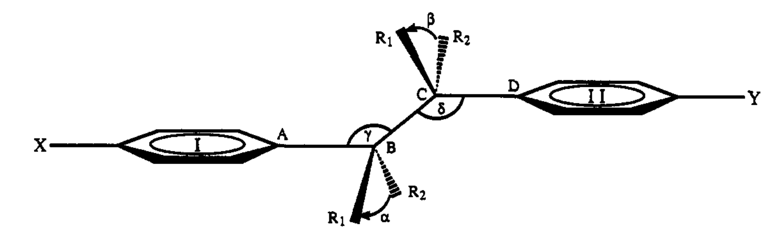
[a] Standard deviations of the least significant digits are shown in parentheses. [b] References 13 and 15. [c] Reference 13. [d] Reference 14.

included. The ORTEP drawings of the solved structures are shown in Figures 1–6 and the crystal packing of **1d** is presented in Figure 7.

In all of the compounds reported here, the remarkable bond lengths between the benzylic carbons are mostly due to repulsions between vicinal substituents in the benzylic positions. The sum of the van der Waals radii for two carbon atoms or two hydrogen atoms is 3.60 and 2.4 Å, respectively. In **1b**, for example, there are 24 nonbonding[16] carbon–carbon bond distances and 32 nonbonding[16] hydrogen–hydrogen distances smaller than the sum of their van der Waals radii. A very similar situation is found in all other compounds studied. These interpenetrations of the electron density must lead to highly repulsive forces. Most of these repulsive interactions are found around the methylene groups directly attached to the benzylic carbons. In fact, several of the shortest nonbonding distances (3.18–3.02 Å for C–C and 2.20–2.01 Å for H–H distances) are observed between the side-chains atoms. These interactions cannot be easily relieved by distortions of bond angles. Such distortions would only aggravate the steric repulsions somewhere else in the molecule, since the already short nonbonding distances are also observed between the chain atoms and the ring atoms, as well as between the remote atoms on geminal substituents. Although some small distortions in bond angles are present, the stretching of the central C–C bond, expected to be an energetically expensive way to deviate from the ideal geometry, is apparently unavoidable.

(15) Beckhaus, H.-D. *Chem. Ber.* **1983**, *116*, 86 and references therein.
(16) Distances between geminal atoms are not included in the count.

Table II. Bond Angles and Torsional Angles around Quaternary Carbons in Substituted Diphenylethanes[a]



	α	β	γ	δ	B–C–R_x R_1	B–C–R_x R_2	C–B–R_x R_1	C–B–R_x R_2	A–B–C–D	I/B–C[b]	II/C–B[b]
1a	104.8	104.8	107.0	107.9	111.1	111.1	111.1	111.1	179.7	c	c
1a	108.5	108.7	109.3	109.0	111.0	111.7	110.8	111.9	164.0	c	c
1a	109.4	109.4	109.6	109.6	108.3	111.2	108.3	111.2	180.0	c	c
1b	108.3	107.3	108.2	108.7	110.5	112.2	111.1	113.4	70.6	88.3	88.8
1c	107.8	107.8	108.8	108.8	113.3	110.4	113.3	110.4	73.7	89.2	89.2
1d	107.1	108.1	110.3	108.5	111.5	111.1	111.3	110.8	174.0	82.1	85.6
1d	107.7	107.6	108.4	108.6	113.3	110.7	110.8	112.0	173.6	93.8	84.0
2a	105.1	105.1	108.2	108.2	112.9	113.1	112.9	113.1	180.0	c	c
2a	107.4	107.4	108.7	108.7	111.6	111.9	111.6	111.9	179.4	86.1	86.1
2b	108.0	108.0	108.3	108.3	111.3	111.2	111.3	111.2	168.1	82.8	82.8
2c	107.2	107.2	108.9	108.9	111.0	110.9	111.0	110.9	166.6	82.8	82.82
3a	103.7	103.7	111.2	111.2	111.2	111.7	111.2	111.7	180.0	c	c
3b	107.2	106.4	110.3	110.6	109.8	113.1	110.6	112.6	91.6	81.9	74.8

[a] The standard deviations for all angles are less than 0.9°; typically 0.5°. [b] The torsional angles between the aromatic planes and central C–C bonds. [c] Not available.

Table III. Summary of Data Collection and Structure Refinement Parameters

	1b	1c	1d	2b	2c	3b
molecular formula	$C_{22}H_{29}NO_2$	$C_{22}H_{28}N_2O_4$	$C_{24}H_{34}N_2O_2$	$C_{30}H_{45}NO_2$	$C_{30}H_{44}FNO_2$	$C_{22}H_{29}NO_2$
space group	$P2_1/n$	$C2/c$	$P2_1$	$C2/c$	$C2/c$	$P2_12_12_1$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorombic
cell dimensions:						
a (Å)	10.665 (5)	21.115 (5)	11.918 (3)	14.438 (8)	14.528 (3)	9.411 (6)
b (Å)	15.305 (5)	10.277 (2)	11.808 (4)	12.451 (4)	12.474 (2)	12.194 (3)
c (Å)	11.534 (5)	10.648 (4)	16.127 (4)	15.718 (8)	15.777 (6)	16.412 (3)
β (deg)	94.01 (3)	118.03 (2)	110.26 (2)	103.01 (4)	103.33 (2)	–
V (Å^3)	1878.0	2029.6	2129.1	2753.2	2782.2	18885.6
Z	4	4	4	4	4	4
D^{cal} (g cm^{-3})	1.201	1.258	1.193	1.090	1.121	1.196
ω scan width (deg)	1.00 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ	0.80 + 0.35 tan θ
scan speed (deg min^{-1})	1.27–5.5	0.61–2.75	1.0–5.5	0.78–2.35	1.65–2.35	1.15–3.3
crystal decay	0.9%	none	none	0.57%	0.50%	6.4%
unique data measured	1746	1783	3117	2420	445	1901
R, R_w	0.052, 0.064	0.046, 0.071	0.064, 0.095	0.076, 0.108	0.082, 0.120	0.037, 0.046
goodness of fit, S	1.920	2.077	1.806	2.048	2.466	1.837

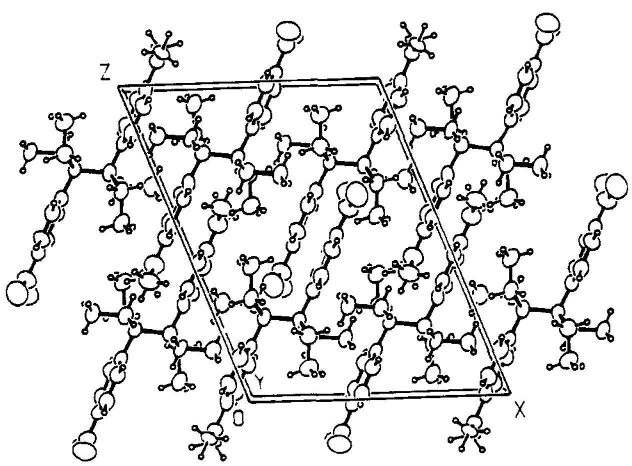


Figure 7. Crystal packing for 3,4-diethyl-3-(4′-nitrophenyl)-4-(4″-(dimethylamino)phenyl)hexane (**1d**).

The consequences of crowding around the central C–C bond are also visible in "remote" parts of the molecule. As pointed out by Osawa,[2,11] the conformation of the butyl side groups in **2a** is far from ideal. A similar situation is found in **2b** and **2c**. All these compounds have strong 1,5-nonbonding repulsions between β-methylenes, and several angles between the side chain carbons are significantly enlarged (up to 120° from the usual tetrahedral angle).

Due to the crowding around the central C–C bonds, the conformational freedom is quite limited for these compounds. The structures of all compounds are very similar. In general, they all have long benzylic C–C bonds, only slightly elongated C–C bonds in side chains, and slightly distorted bond angles around the center of the molecule. The angles between the geminal alkyl substituents (α,β) are slightly smaller than tetrahedral (on average 107.8° ± 0.8°). This angle contraction allows the "halves" of the molecule to avoid each other both by elongation of the central C–C bond and by opening of the bonds between the vicinal substituents (B–C–R_x and C–B–R_x, average 111.4° ± 1.2°).

These structural features are well modeled by molecular mechanics.[13,15] Although the calculated α and β angles are clearly too small, the contracting trend is correctly predicted for these angles, as is the angle-opening trend for the angles between vicinal substituents. Even the central bond lengths are off by less than 0.035 Å. Taking into account the uncertainty of the experimental determination of the bond lengths and angles, the predictions are quite impressive.

The interesting difference between the compounds is in the relative conformational position of the aryl substituents. Molecular mechanics calculations predict the anti conformation to be the most stable.[13] Such a conformation is indeed found in 7 out of 10 cases presented here (A–B–C–D angle, Table II). In the remaining cases the phenyls are gauche with the torsional angle significantly more than 60°. Molecular mechanics calculations[13] on the parent hydrocarbons estimate that the energy of the gauche conformation is less than 1.2 kcal/mol higher than that of the anti conformation. Crystal packing forces may easily account for the observed differences in the conformation. For especially crowded molecules such as **3b**, MM2 predicts[13] two local gauche minima of essentially identical energy, symmetrically disposed around the ideal 60° angle. One of these minima may, in fact, be represented by the structure found for **3b**.

In all compounds, both phenyl rings are appropriately disposed for maximum interactions between the π-systems and the central σ-bonds. The torsional angles between the ring planes and these bonds deviate at most by 10° from the ideal 90° angle (with the exception of one ring in **3b**). This assures that any substituent effects on the length of the central bond due to σ-π interactions should be maximized in these compounds. However, within experimental error, *there is no difference in the bond length between differently substituted 1 or 2*. Even the strongly electron withdrawing nitro group has no apparent effect on the structure of these compounds.

Interestingly, the prediction made by Osawa[11] that push–pull substituted diphenylethanes will have the longest bonds is not supported by the data obtained for **1d**. It can be argued that charge-transfer interactions in **1d** have diminished the donor and acceptor character of these substituents. However, such interactions are generally quite weak. In addition, the crystal packing of **1d** (Figure 7) indicates that the shortest phenyl stacking distances are between the *p*-nitrophenyl rings and *p*-(dimethylamino)phenyl rings, but not between the two kinds of rings.

It appears that the length of the central C–C bond is mostly affected by the steric congestion in the center of the molecule. The potential conjugation of the σ-bonds with phenyl rings may have an additional effect on the bond elongation,[2,10] but this effect is not necessary to produce C–C bonds longer than 1.62 Å (Scheme I, structure d). The adjustment of the electronic demand of the phenyl groups by substitution, including strong electron-withdrawing substituents and push–pull substitution patterns, has no detectable effect on these remarkably long C–C bonds.

Experimental Section

General. ^{1}H NMR spectra were taken on Varian EM-360 (60 MHz), Bruker WP-200 (200 MHz), Bruker AM-300 (300 MHz), and Bruker AM-360 (360 MHz) instruments. ^{13}C NMR spectra were recorded on the Bruker WP-200 (50.3 MHz), Bruker AM-300 (75.5 MHz), and Bruker AM-360 (90.6 MHz) instruments. Chemical shifts are reported in ppm referenced to Me_4Si. Infrared (IR) spectra were obtained using a Perkin-Elmer Model 281B infrared spectrometer. All samples were thin films on NaCl plates. Absorption peaks are reported in cm^{-1}. Mass spectra were taken on a Kratos MS 9/50 doublefocusing spectrometer in electron impact (EI) or chemical ionization (CI) mode. Only structurally significant peaks, or those with a relative intensity greater than 10% of the base peak, are reported. Preparative flash chromatography was performed with Machery Nagel silica gel 60, 230–400 mesh. Preparative HPLC was carried out on a Rainin Rabbit HP/HPX system equipped with Knauer variable-wavelength monitor, and 21.4 mm i.d. × 25 cm long, 8-μm silica column. For all runs, Aldrich or J. T. Baker HPLC solvents were used at a flow rate of 22 mL/min.

For all the structures, accurate cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation. The details of data collection are summarized in Table III. The structures were solved by direct method software. Final atomic coordinates, geometrical parameters, and anisotropic thermal parameters for **1b**, **1c**, **1d**, **2b**, **2c**, and **3b** are included in the supplementary material.

Synthesis. 3,4-Diethyl-3,4-diphenylhexane (**1a**), 5,6-dibutyl-5,6-diphenyldecane (**2a**), and 2,3,4,5-tetramethyl-3,4-diphenylhexane (**3a**) were prepared by the procedure of Rüchard et al.[13] The crude hydrocarbons were nitrated as described below to yield mono and dinitro derivatives.

3,4-Diethyl-3-(4′-nitrophenyl)-4-phenylhexane (1b). To a stirred solution of **1a** (5.0 g, 0.017 mol) in 100 mL of acetic anhydride was added 3 molar equiv of concentrated nitric acid (3.5 mL, 0.050 mol). The nitric acid was added slowly so as to maintain the temperature of the solution near room temperature. After about 2 h, TLC analysis with 50% hexane–50% CH_2Cl_2 eluant showed three major spots corresponding to starting material (R_f 0.90), mononitrated product (R_f 0.65), and dinitrated product (R_f 0.40). The reaction mixture was poured into a large volume of ice–water (500 mL) and stirred until the acetic anhydride was completely hydrolyzed. The organic residue was extracted into hexane (2 × 200 mL) and washed twice with saturated aqueous $NaHCO_3$ and once with water. The hexane layer was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. Separation by flash column chromatography (hexane/CH_2Cl_2 gradient) and crystallization in absolute ethanol afforded the desired **1b** in approximately 20% yield (1.1 g, 0.003 mol), mp 81–83 °C. From the same reaction mixture the more polar 3,4-diethyl-3,4-bis(4′-nitrophenyl)hexane (**1c**) was isolated in 30% yield; mp 105–106 °C after recrystallization from ethanol.

1b: ^{1}H NMR (360 MHz, $CDCl_3$) 7.97 (d, J = 9.0 Hz, 2 H), 7.12 (m, 3 H), 7.02 (d, J = 9.0 Hz, 2 H), 6.87 (m, 2 H), 2.11 (m, 2 H), 2.00 (m, 6 H), 0.73 (t, J = 8.0 Hz, 6 H), 0.71 (t, J = 8.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) 153.1, 145.3, 143.3, 130.7, 129.7, 126.5, 125.5, 121.2, 52.6, 51.9, 25.3, 25.1, 10.4, 10.3. IR: 3080, 3050, 2970, 2940, 2880, 1600, 1590, 1510, 1455, 1370, 1335, 1175, 1120, 1090, 1065, 1035, 1020, 995, 835, 810, 735, 705, 685; MS-EI (m/e, relative intensity) 310 (P$^+$ – Et, 1), 240 (2), 193 (36), 147 (48), 117 (11), 115 (8), 105 (76), 91 (100), 77 (4).

1c: ^{1}H NMR (360 MHz, $CDCl_3$) 8.02 (d, J = 9.0 Hz, 4 H), 7.05 (d, J = 9.0 Hz, 4 H), 1.94–2.15 (m, 8 H), 0.75 (t, J = 7.28 Hz, 12 H); ^{13}C NMR (90.6 MHz, $CDCl_3$) 152.0, 145.7, 130.6, 121.5, 52.7, 25.5, 10.2; MS-EI (m/e, relative intensity) 355 (P$^+$ – Et, 2), 337 (2), 326 (P$^+$ – 2Et, 13), 308 (11), 296 (8), 193 (100), 176 (5), 164 (15), 161 (6), 150 (91), 146 (18), 136 (33), 131 (19), 120 (11), 116 (23), 106 (12), 104 (17), 91 (15), 78 (12).

3,4-Diethyl-3-(4′-nitrophenyl)-4-[4″-(dimethylamino)phenyl]-hexane (**1d**) was prepared by partial reduction of **1c**, followed by N-methylation. **1c** (240 mg, 0.625 mmol) was dissolved in 100 mL of ethanol, then treated with approximately 250 mg of 10% Pd/C catalyst and 3 equiv of hydrazine monohydrate (91 μL, 1.88 mmol). The mixture was refluxed for 20 min and filtered to remove the catalyst, and the solvent was evaporated in vacuo. The residue was dissolved in dichloromethane, washed with water, and dried over sodium sulfate, and the solvent was removed once again. Flash column chromatography using a hexane–ethyl acetate gradient yielded starting material, monoamino–mononitro product, and bisamino products in roughly 1:2:1 ratio.

The monoamino compound, 3,4-diethyl-3-(4′-nitrophenyl)-4-(4″-aminophenyl)hexane (77.8 mg, 0.22 mmol), was dissolved in 7 mL of acetonitrile and treated with 37% formaldehyde/water (187 μL, Fisher), sodium cyanoborohydride (41 mg), and glacial acetic acid (23 μL). After 3.5 h, a second portion of acetic acid (23 μL) was added, and stirring was continued for 0.5 h. The reaction mixture was then diluted with 30 mL of ether and washed twice with 1 M KOH solution and once with brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The residue was purified by column chromatography using petroleum ether/ethyl acetate eluant (9:1, R_f = 0.7). Crystallization from ethanol gave orange crystals of 3,4-diethyl-3-(4-nitrophenyl)-4-[4-(dimethylamino)phenyl]hexane (**1d**) in 60% yield, mp 105–106 °C. The crystals for the X-ray analysis were grown from acetonitrile.

1d: ^{1}H NMR (360 MHz, $CDCl_3$) 7.97 (d, J = 9.0 Hz, 2 H), 7.04 (d, J = 9.0 Hz, 2 H), 6.71 (d, J = 8.5 Hz, 2 H), 6.52 (d, J = 8.5 Hz, 2 H), 2.92 (s, 6 H), 2.10 (m, 2 H), 1.96 (m, 6 H), 0.73 (t, J = 8.2 Hz, 12 H); ^{13}C NMR (125.8 MHz, $CDCl_3$) 153.6, 148.2, 145.2, 131.0, 130.6, 130.4, 121.1, 110.6, 52.9, 51.2, 40.4, 25.5, 25.4, 10.5, 10.4; MS-EI (m/e, relative intensity) 353 (P^+ – Et, 0.5), 335 (2), 324 (2), 306 (14), 190 (100), 175 (6), 162 (17), 160 (41), 148 (8), 145 (13), 144 (11), 136 (10), 134 (13), 130 (10), 116 (16), 91 (9), 77 (6); MS-CI (CH_4, m/e, relative intensity) 228 (3), 218 (2), 190 (100), 174 (4), 162 (20).

5,6-Dibutyl-5-(4′-nitrophenyl)-6-phenyldecane (**2b**) was prepared by nitration of **2a** in acetic anhydride as described for **1b** above. The column-purified product crystallized from ethanol to fine colorless crystals: mp 85–86 °C; ^{1}H NMR (360 MHz, $CDCl_3$) 7.96 (d, J = 9.0 Hz, 2 H), 7.13 (m, 3 H), 7.01 (d, J = 9.0 Hz, 2 H), 6.86 (m, 2 H), 1.97 (m, 2 H), 1.88 (m, 6 H), 1.26 (m, 8 H), 1.08 (m, 2 H), 0.98 (m, 6 H), 0.84 (m, 12 H); IR 3045, 2935, 2855, 1590, 1500, 1445, 1360, 1330, 1085, 830, 740, 710, 680; MS-EI (m/e, relative intensity) 365 (9), 347 (7), 249 (10), 203 (20), 163 (12), 147 (25), 133 (20), 118 (41), 105 (19), 91 (100), 57 (11).

Preparation of 5,6-dibutyl-5-(4-nitrophenyl)-6-(3-fluorophenyl)decane (**2c**) was analogous to that described for **2b**. An equimolar mixture of 5-phenylnonan-5-ol and 5-(3-fluorophenyl)nonan-5-ol (each prepared from 5-nonanone and the corresponding phenylmagnesium bromide) were coupled using the procedure described for **1a**.[13] The crude mixture, including the 5,6-dibutyl-5-phenyl-6-(3-fluorophenyl)decane cross-coupling product, was nitrated in acetic anhydride as described above. Flash column chromatography using CH_2Cl_2–hexane (1:9), followed by HPLC separation with 100% hexane, afforded pure **2c**. Crystallization from ethanol at room temperature gave colorless crystals: mp 104.5–105.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.98 (d, J = 9.0 Hz, 2 H), 7.04 (d, J = 9.0 Hz, 2 H), 7.00–7.15 (m, 1 H), 6.85 (m, 1 H), 6.60 (m, 2 H), 1.75–2.04 (m, 8 H), 1.27 (m, 8 H), 0.85–1.12 (m, 8 H), 0.85 (m, 12 H); IR 3065, 2925, 1930, 1800, 1585, 1505, 1450, 1365, 1330, 1250, 1220, 1205, 1150, 1090, 995, 935, 870, 835, 760, 715, 685; MS-EI (m/e, relative intensity) 423 (3), 383 (9), 365 (24), 325 (8), 309 (7), 249 (15), 221 (13), 215 (8), 165 (17), 163 (35), 151 (16), 146 (13), 136 (36), 133 (12), 129 (14), 123 (27), 115 (17), 109 (100), 91 (16), 69 (10).

2,3,4,5-Tetramethyl-3,4-diphenylhexane (**3a**) obtained as ca. 1:1 mixture of *meso* and *dl* isomers was nitrated by the procedure indicated for **1b**. The resulting yellow oil was submitted multiple times to flash column chromatography (hexane/CH_2Cl_2 gradient, or hexane/ethyl acetate gradient), but could not be separated cleanly. Repeated preparative HPLC (70% hexane–30% CH_2Cl_2) was finally successful in affording pure *erythro* and *threo* isomers, of which only the *threo* crystallized (colorless crystals from ethanol, mp 115–117 °C). *erythro*-**3b**: ^{1}H NMR (360 MHz, $CDCl_3$) 7.89 (d, J = 9.0 Hz, 2 H), 7.12 (m, 4 H), 6.80–7.00 (br, 3 H), 2.87 (sep, J = 6.5 Hz, 2 H), 1.42 (s, 3 H), 1.27 (s, 3 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.19 (d, J = 6.5 Hz, 3 H), 0.47 (d, J = 6.5 Hz, 3 H), 0.41 (d, J = 6.5 Hz, 3 H); MS-EI (m/e, relative intensity) 226 (5), 193 (29), 147 (100), 131 (14), 117 (12), 115 (13), 105 (70), 103 (10), 91 (77), 77 (11). *threo*-**3b**: ^{1}H NMR (360 MHz, $CDCl_3$) 8.13 (d, J = 9.0 Hz, 2 H), 7.60 (d, J = 9.0 Hz, 2 H), 7.21–7.40 (m, 5 H), 1.70 (m, 1 H), 1.62 (m, 1 H), 1.53 (s, 3 H), 1.50 (s, 3 H), 1.10 (d, J = 6.0 Hz, 3 H), 1.05 (d, J = 6.0 Hz, 3 H), 0.36 (d, J = 6.0 Hz, 3 H), 0.28 (d, J = 6.0 Hz, 3 H); MS-EI (m/e, relative intensity) 312 (6), 249 (6), 226 (4), 193 (20), 150 (16), 147 (83), 131 (40), 117 (24), 115 (20), 105 (92), 103 (20), 91 (100), 84 (15), 77 (20), 69 (21).

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Supplementary Material Available: Final atomic coordinates, bond lengths, bond angles, torsional angles, and anisotropic thermal parameters for **1b**, **1c**, **1d**, **2b**, **2c**, and **3b** as well as NMR spectra of these compounds (60 pages); listing of observed and calculated structure factors (91 pages). Ordering information is given on any current masthead page.

Gas-Phase Chemistry of the Negative Ions Derived from Azo- and Hydrazobenzene

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The proton affinities of the azobenzene radical anion and the conjugate base of hydrazobenzene have been determined to be 1465 kJ mol^{-1} and 1514 kJ mol^{-1}, respectively, with the use of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source. The proton affinities lead in combination with a measured electron affinity of azobenzene (55 kJ mol^{-1}) to a N–H bond dissociation energy (BDE) of 306 kJ mol^{-1} for hydrazobenzene while the N–H BDE of the PhNHṄPh radical is estimated to be 208 kJ mol^{-1}. The difference between the N–H BDE values of 98 kJ mol^{-1} approximates the π-bond energy of the nitrogen–nitrogen bond in azobenzene. The reaction of the PhṄN̄Ph and PhNHN̄Ph ions with derivatives of trifluoroacetic acid are characterized. The occurrence of dissociative electron transfer instead of S_N2 substitution in reactions of the azobenzene radical anion with halogen-substituted methanes is discussed.

Introduction

The formation and reactivity of organic radical anions in the condensed phase is studied intensely,[1-5] whereas less is known about the gas-phase ion/molecule chemistry of these species. The reports are focused mainly on the determination of positive or negative electron affinities (EA) and rate constants for exothermic electron-transfer reactions.[6-14] Positive electron affinities are reported for

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