Geometry at the aliphatic tertiary carbon atom: computational and experimental test of the Walsh rule

**Stanislav Böhm[a] and Otto
Exner[b]***

[a]Department of Organic Chemistry, Prague
Institute of Chemical Technology, 16628 Praha
6, Czech Republic, and [b]Institute of Organic
Chemistry and Biochemistry, Academy of
Sciences of the Czech Republic, 16610 Praha 6,
Czech Republic

Correspondence e-mail: exner@uochb.cas.cz

The geometrical parameters of molecules of 2-substituted 2-methylpropanes and 1-substituted bicyclo[2.2.2]octanes were calculated at the B3LYP/6-311+G(d,p) level. They agreed reasonably well with the mean crystallographic values retrieved from the Cambridge Structural Database for a set of diverse non-cyclic structures with a tertiary C atom. The angle deformations at this C atom produced by the immediately bonded substituent are also closely related to those observed previously in benzene mono derivatives (either as calculated or as derived from crystallographic data). The calculated geometrical parameters were used to test the classical Walsh rule: It is evidently true that an electron-attracting substituent increases the proportion of C-atom p-electrons in the bond to the substituent and leaves more s-electrons to the remaining bonds; as a consequence the C—C—C angles at a tertiary carbon are widened and the C—C bonds shortened. However, this rule describes only part of the reality since the bond angles and lengths are controlled by other factors as well, for instance by steric crowding. Another imperfection of the Walsh rule is that the sequence of substituents does not correspond to their electronegativities, as measured by any known scale; more probably it is connected with the inductive effect, but then only very roughly.

1. Introduction

Small changes in geometry caused by substitution have been investigated with two main purposes:

(i) standard reference values for classes of compounds can be obtained; deviations from these values can be attributed to packing forces in the given crystal structure.

(ii) Changes in bond angles and lengths can be correlated with the various properties of the substituents to investigate which property they are controlled by.

The substituent effects in the ground state of neutral molecules are generally less regular and have been studied (Topsom, 1987) less than the effects on acid–base properties and kinetics.

Until now, only the benzene derivatives denoted as (1) below have received systematic attention. This was because of, on the one hand, the importance of these compounds and the availability of their structures and, on the other hand, by the theoretical interest in the extent of conjugation (resonance) of the individual substituents. Domenicano and co-workers (Domenicano *et al.*, 1975*a*,*b*; Domenicano & Vaciago, 1979) and Norrestam & Schepper (1978, 1981) independently evaluated statistically the available X-ray structures; both groups agree that only the effects on the bond angles can be determined reliably. The possibilities of this approach were criti-

cally appraised by Krygowski (1990). Quantum chemical calculations at the present level may yield both reliable bond angles and lengths. The most significant result was good agreement between crystallographic and calculated angles (Exner & Böhm, 2002a), also including the deviation of structure (1) from C_{2v} symmetry in the case of unsymmetrical X substituents, the so-called AGIBA effect (Krygowski et al., 1996). However, there is a serious disagreement concerning the interpretation of the geometrical parameters and their relation to other quantities. The α angle in (1) was connected with the substituent electronegativity (Domenicano et al., 1975b; Krygowski, 1990) or the σ-electron density (Krygowski et al., 1986) or merely s-electron density (Krygowski, 1990) according to the qualitative Walsh rule (Walsh, 1947). The γ and δ angles were correlated with resonance (Domenicano & Murray-Rust, 1979) or with the π-electron density (Krygowski et al., 1986). However, none of these correlations was confirmed when a broader set of calculated data was used (Exner & Böhm, 2002a). Most recently, Campanelli et al. (2003) derived two linear functions of the angles α–δ, on the basis of lower-level calculations and neglecting the AGIBA effect: one related to electronegativity and the other to resonance.
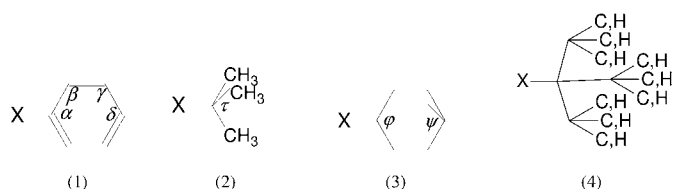
and the bond angles φ and ψ in 21 derivatives of bicyclo[2.2.2]octane (3) within the framework of the density functional theory at the same computational level as previously used (Exner & Böhm, 2002a). Comparison with the experimental data was possible with the general acyclic structure (4), although an exact agreement was not expected due to some steric hindrance in (4) which is not present in (2). Returning to the two purposes mentioned at the beginning, that under (i) must be modified in our case. Our bond angles and bond lengths can be hardly used as reference values for evaluating the packing forces since the structures compared will always differ. However, they can serve to estimate the steric hindrance in the structures (4) and − probably more important − the effect of ring closure in structures similar to (4) in which two or all three branches are connected to form six-membered or smaller rings.

2. Calculations

DFT calculations were performed at the B3LYP/6-311+G(d,p) level using the GAUSSIAN03 program of Frisch et al. (2003). Full geometry optimization and a vibrational analysis were carried out in all cases. In questionable cases, the optimization was started from alternative initial structures representing the anticipated, less populated conformations. The calculated geometrical parameters are listed in Tables 1 and 2. The minimum-energy conformations and energies of some compounds have already been reported in connection with other problems (Exner & Böhm, 2002b).

A search of the Cambridge Structural Database (CSD) was carried out using Version 5.24 (November 2002, 272 066 entries). The structures of (4) were retrieved with two constraints: the R factor < 0.05 and all atoms with atomic weights less than 36. Subsequently, all the structures with a ring closure between two branches were excluded. The three C—C—C angles in each compound were averaged; from the averaged angles in all compounds the median value was taken. These values are given in Table 1, column 5, together with the number of hits from which they were derived.

In our opinion, the above discussion has become too sophisticated and more significant progress can be expected from comparison with simpler model compounds that do not include any π-electrons. We have calculated here the bond angles τ and bond lengths l_{C-C} in 21 tert-butyl derivatives (2)

3. Results and discussion

3.1. Calculated and crystallographic bond angles

The only significant comparison possible was between the calculated angle τ in the isolated molecules of 2-substituted 2-methylpropanes (2) and the same angle in the crystal structures of the more complex derivatives (4), in which steric hindrance is possible but no ring closure is present. The main problem is that the three C—C—C angles in (2) are unequal in most derivatives, differing in some cases by several degrees. A less important difficulty was that acyclic structures with certain substituents were completely absent in the CSD or were represented by only a few examples (Table 1, column 6, the numbers in brackets). Considering these difficulties, the agreement between columns 4 and 5 of Table 1 is quite good. We anticipated τ being larger in (4) than in (2) because of
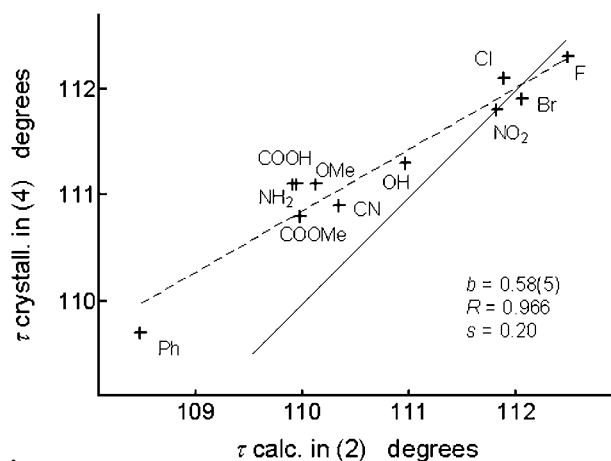

Figure 1
Relationship between the calculated bond angle τ in the tert-butyl derivatives (2) and the corresponding crystallographic angle in the general structure (4); the full line represents $y = x$; the broken line represents the regression line.

Table 1
Calculated and crystallographic bond angles in monosubstituted 2-methylpropanes (2) and bicyclo[2.2.2]octanes (3).

Σs: s-electron density at the C atom of $C(H_3)$ according to Mulliken (1955); τ cryst.: median values in the structure of (4) obtained from the CSD (the number of hits retrieved are given in square brackets); benzenes, α in (1): Exner & Böhm (2002a), except the last three values calculated in this work.

| Substituent | 2-Methylpropanes | | | | | Bicyclooctanes | | Benzenes, |
	l_{C-C} in (2)	Σs	τ in (2)	τ cryst.		φ in (3)	ψ in (3)	α in (1)
H	1.534	3.349	111.13			109.29	109.29	120.00
CH_3	1.540	3.346	109.48			108.16	109.82	118.17
^tBu	1.546	3.349	107.38		[0]	106.86	110.41	117.30
Ph	1.545	3.384	108.48	109.7	[51]	107.66	110.02	118.15
CH_2Cl	1.540	3.350	109.69		[0]	108.49	109.80	119.00
CF_3	1.541	3.356	110.25		[0]	109.03	109.79	120.40
CHO	1.541	3.292	110.56		[0]	108.85	109.08	119.84
COOH	1.542	3.351	109.95	111.1	[3]	108.85	109.79	119.90
$COOCH_3$	1.541	3.349	109.98	110.8	[13]	108.79	109.81	119.74
CN	1.545	3.353	110.34	110.9	[11]	109.00	109.71	120.02
NO_2	1.530	3.358	111.82	111.8	[9]	110.09	109.81	122.36
NH_2	1.539	3.345	109.91	111.1	[3]	108.45	109.78	118.59
$N(CH_3)_2$	1.543	3.349	108.59		[0]	107.48	110.31	117.28
OH	1.533	3.349	110.96	111.3	[130]	109.14	109.77	120.12
OCH_3	1.534	3.350	110.13	111.1	[8]	108.81	109.99	119.83
F	1.524	3.358	112.48	112.3	[4]	110.25	109.77	122.57
Cl	1.526	3.348	111.88	112.1	[11]	110.18	109.81	121.40
Br	1.525	3.347	112.05	111.9	[3]	110.26	109.82	121.45
COO^-	1.537	3.331	109.48			108.16	109.97	118.33
O^-	1.571	3.333	107.04			105.63	109.76	113.78
NH_3^+	1.528	3.371	112.54			110.69	109.56	123.33

steric overcrowding in some structures (4). It is actually larger, but not equally so, for all X groups and not in accordance with their steric requirement: Smaller angles are widened more (Fig. 1), whilst larger angles are more resistant. Irrespective of these deviations, the calculated angles τ can serve as reference values against which the deformations in the individual molecules are measured.

3.2. Intercorrelations of the geometrical parameters

The close similarity of the φ angle in (3) and τ in (2) was expected (Table 3, line 1); ring closure makes φ smaller than τ

$b = 1.71(8)$
$R = 0.978$
$s = 0.44$
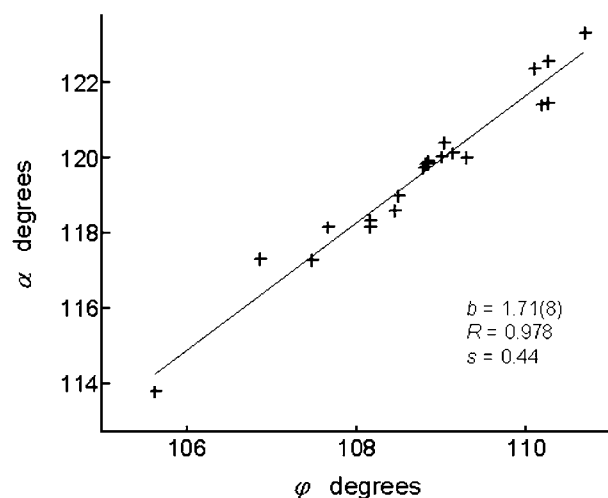
Figure 2
Relationship of the calculated bond angles α in substituted benzenes (1) and the φ angle in 1-substituted bicyclo[2.2.2]octanes (3).

and less variable. On the other hand, close correlation between the α angle in substituted benzenes (1) and the angles in the aliphatic derivatives (2) and (3) was not expected, at least not too close (Table 3, lines 2 and 3; Fig. 2). Sensitivity to substitution is greater in aromatic derivatives, but no other effect of the π electrons was observed. This is a confirmation of the opinion of Domenicano & Vaciago (1979) that the α angle in benzene derivatives is controlled by the σ-electron density.

When explaining the variance of the α angle in (1), Krygowski (1990) referred to the Walsh rule (Walsh, 1947; Bent, 1961). According to this rule, the bond to an electronegative substituent preferentially uses C-atom p-electrons and leaves a greater contribution of the s-character to the other bonds from the same C atom. When this substituent is situated at a tertiary carbon, the three C—C bonds acquire more s-character than in idealized sp^3 hybridization: the C—C—C angles are therefore widened and the C—C bonds shortened. The crucial test may be the dependence of the average angle τ on the average bond length l_{C-C} (Fig. 3). A rough relation cannot be doubted; a linear relation has not been assumed. (The point for ^tBu may deviate for steric reasons.) However, the succession of points does not agree with any known scale of electronegativity, see §3.3.

In contrast to the obvious relationships between the angles τ, φ and α, we found no clear relationships for the angle ψ in (3) with either φ in the same compounds or with δ in (1). In disubstituted bicyclo[2.2.2]octanes (5), the simultaneous action of the two substituents can be evaluated according to the distance r of the non-bonded atoms $C1 \cdots C4$ (Table 2). We found no other relationship than the additive character of r with respect to the substituents X and Y. It can be expressed

Table 2
Calculated interatomic distances C1···C4 in disubstituted bicyclo[2.2.2]octanes (5).

	H	CH$_3$	CH$_2$Cl	COOH	CN	NO$_2$	NH$_2$	OH	Cl	COO$^-$	O$^-$	NH$_3^+$
H	2.599	2.627	2.618	2.609	2.603	2.576	2.618	2.559	2.576	2.632	2.697	2.557
CH$_3$	2.627	2.652	2.647	2.637	2.632	2.603	2.645	2.627	2.606	2.658	2.721	2.587
CH$_2$Cl	2.618	2.647	2.635	2.630	2.623	2.601	2.639	2.620	2.599	2.649	2.713	2.581
COOH	2.609	2.637	2.630	2.620	2.615	2.587	2.629	2.610	2.590	2.642	2.708	2.569
CN	2.603	2.632	2.623	2.615	2.610	2.582	2.624	2.606	2.588	2.634	2.701	2.568
NO$_2$	2.576	2.603	2.601	2.587	2.582	2.554	2.596	2.578	2.558	2.606	2.672	2.540
NH$_2$	2.618	2.645	2.639	2.629	2.624	2.596	2.637	2.619	2.598	2.648	2.711	2.582
OH	2.559	2.627	2.620	2.610	2.606	2.578	2.619	2.600	2.580	2.629	2.692	2.564
Cl	2.576	2.606	2.599	2.590	2.588	2.558	2.598	2.580	2.560	2.599	2.662	2.548
COO$^-$	2.632	2.658	2.649	2.642	2.634	2.606	2.648	2.629	2.599	2.681	2.740	2.567
O$^-$	2.697	2.721	2.713	2.708	2.701	2.672	2.711	2.692	2.662	2.740	2.736	2.638
NH$_3^+$	2.557	2.587	2.581	2.569	2.568	2.540	2.582	2.564	2.548	2.567	2.638	2.547

simply as the dependence on the sum of the angles φ and ψ, Table 3, line 4.

(5)
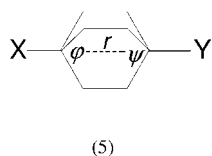
3.3. Bond angles and substituent parameters

The values of geometrical parameters were correlated with the parameters expressing some defined or anticipated properties of substituents: inductive constants σ_I (Charton, 1981), steric constants υ (Charton, 1991), polarizability (σ_α) and electronegativity constants (σ_χ) (Taft & Topsom, 1987), electronegativity χ (Huggins, 1953) of the first atom of the substituent, group electronegativities as suggested by Wells (1968), Inamoto & Masuda (1982) or Altona *et al.* (1989); even correlation with the calculated energy of compounds (2) or (3)
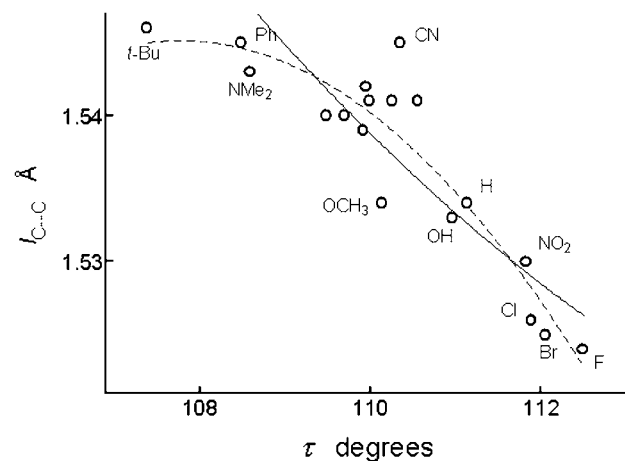
was attempted. Many multiple regressions with combinations of these parameters were also examined using the methods of ascending and descending regression. All this was done either with all substituents of Table 1 or excluding the three charged groups since some parameters are not known for charged groups. No simple and significant correlation was found. The most significant correlations of τ or φ were with σ_I and υ (charged groups not included), see Table 3, lines 5 and 6. Although very rough, these correlations seem to have some rationale: the inductive effect makes the angles larger (Walsh rule) and the steric effect smaller; φ situated in a rigid system is less sensitive to changes than τ. Nevertheless, it is evident that these angles are also controlled by factors other than the inductive and steric factors. Some improvement can be achieved by introducing the polarizability σ_α, but the significance is low. Correlations of the bond lengths l_{C-C} are significantly worse than those of τ.

Particular attention was given to the correlation with electronegativity. This correlation was required for the α angle in benzene derivatives, in agreement with the Walsh rule (Krygowski, 1990), but not confirmed by us (Exner & Böhm, 2002a); hence it should also be observed with τ or φ. However, we found no correlation of these angles with $\sigma\theta_\chi$ or χ on various scales. The last version of the claimed dependence on

Figure 3
The Walsh rule: the calculated averaged bond lengths l_{C-C} in the *tert*-butyl derivatives (2) plotted *versus* the average bond angles τ. The broken curve represents the quadratic interpolation and the full curve an interpolation without the point ^tBu; some important or deviating substituents X are marked.
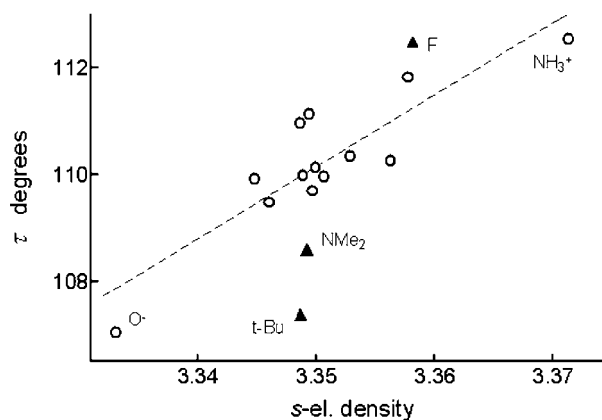

Figure 4
The Walsh rule: plot of the averaged bond angles τ in the *tert*-butyl derivatives (2) *versus* the s-electron density at the CH$_3$ carbon atom; filled triangles denote substituents deviating for different possible reasons.

Table 3
Some important correlations of geometrical parameters in (2)–(5).

Regression coefficients b are given with standard deviations in parentheses; correlation coefficient R, standard deviation from the regression s (angles in $°$, lengths in Å) and the number of data N, respectively.

No.	Response function	Explanatory variables	b		R	s	N
1	φ in (3)	τ in (2)	0.79 (3)		0.982	0.23	21
2	α in (1)	τ in (2)	1.32 (11)		0.943	0.72	21
3	α in (1)	φ in (3)	1.71 (8)		0.978	0.44	21
4	r in (5)	$\varphi + \psi$ in (5)	−0.0246 (6)		0.979	0.0095	78
5	τ in (2)	$\sigma_I \upsilon$	4.0 (9)	−2.4 (7)	0.839	0.77	18
6	φ in (3)	$\sigma_I \upsilon$	3.2 (7)	−1.4 (5)	0.844	0.58	18

electronegativity (Campanelli *et al.*, 2003) refers to the linear function S_E of the four angles α, β, γ and δ in (1). Their results have been made less clear by confusing the fundamental terms 'electronegativity' and 'inductive effect'. With the set of substituents used in this work, we obtained no correlation of the function S_E with σ_χ; correlation with σ_I was poor, not significantly better than the correlation of α alone. With a larger set of substituents, the results were similar. We conclude that the idea of the bond angles being controlled by electronegativity must be abandoned.

Nevertheless, the essence of the Walsh rule is not in the electronegativity, which was not defined exactly by Walsh (1947), but in the rehybridization of s- and p-electrons. We calculated the s-electron density at the CH_3 carbon in (2) according to the procedure of Mulliken (1955), Table 1, column 3, and plotted it *versus* τ (Fig. 4), excluding the substituents with the second-row atoms. The plot for *tert*-butyl deviates, evidently for steric reasons (τ is reduced); the deviation of $N(CH_3)_2$ may be due to similar reasons; the deviation of F is unexplained. The Walsh rule seems to be correct in principle. However, the proof is strongly dependent on the two charged substituents and there is still an additional factor controlling the bond angles. We also calculated the s-electron density according to Löwdin (Szabo & Ostlund, 1982), but the values were quite different with no relation to τ. We obtained no correlation with the other quantities examined: the total electron density at the central C atom or at the CH_3 carbon in (2), or the energy of the $1s$ orbital at the central carbon according to Böhm & Kuthan (1984).

4. Conclusions

In our opinion, the calculated τ angles (and to a lesser extent the φ angles) can serve as reference values to be compared with the crystallographic data of compounds with a tertiary carbon. In particular, the effects of steric hindrance and of ring closure can be estimated in this way. On the other hand, it is difficult at present to explain which physical property controls the geometrical parameters. They show little correlation to the known structure and reactivity parameters, particularly not to the electronegativity; some opposite claims in the literature were mostly a result of the small size of the sets investigated and imprecise statistics. The Walsh rule can explain the general dependence by the sharing of p- and s-electrons, but merely in a qualitative sense. In particular, the dependence is not related to the electronegativity as it is commonly defined.

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