657, a method for estimating tetrahedral bond angles

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A regular tetrahedron has six spatial angles. The sum of these spatial angles for a tetrahedron with all four groups the same (CA_4) is 6 × 109.4712206°. To the nearest degree that value is 657°. For a tetrahedron with one group different (CA_3B), there are two different bond angles. The sum of these two angles can be approximated to be 219°, one third of 657°. For a tetrahedron with disubstitution by the same group (CA_2B_2), the approximate sum involves three different angles: $\angle ACA + \angle BCB + 4\angle ACB = 657°$. For a tetrahedron with disubstitution by two different groups (CA_2BD), the approximate sum uses four different angles: $\angle ACA + \angle BCD + 2\angle ACB + 2\angle ACD = 657°$. For a tetrahedron with all groups different (CABDE), the approximate sum comes from six angles. Examples of each type are given along with the limitations of the method.

Chemists rarely neglect any help to understand the myriad of reactions and structures that are the subjects of their investigations. Nonetheless, 657 has eluded the attention, in particular, of organic chemists whose symbol is often the tetrahedron. It is the tetrahedron that is the source of the 657.

Consider any tetrahedral carbon compound with four of the same atoms, such as methane or carbon tetrachloride. The tetrahedral bond angle for such compounds is usually given as 109.5°. More exactly, it is 109° 28′ or 109.4712°, derived by solid trigonometry as by Bieber,[1] by the law of cosines as shown by Kawa,[2] by the vector algebraic approach of Duffey[3] or through the spherical polars of Glaister.[4] These four atoms make six angles in space with the central carbon. The sum of these angles is 657° or 656.8273°. *We propose that this sum* ("*total angles*") *can be used for the facile estimation of bond angles as the symmetrical tetrahedra undergo substitution.*

Results and discussion

The substitutions can range from one to all four atoms. The five different possibilities are arranged in Table 1. Monosubstitution is designated as CA_3B wherein C represents the central atom, which is usually carbon but may be another tetravalent atom. The two types of disubstitution are given as CA_2B_2 and CA_2BD. All of these forms, as well as that with four different substitutions (CABDE) have six angles whose approximate sum will be 657° or 656.83°. The six angles are made more obvious by examination of Fig. 1.

The methyl halides are examples of CA_3B and their experimental bond angles are listed in Table 2. The total angles in the table were calculated by multiplying each of the two angles by three and then adding these products. For such monosubstituted tetrahedra, predictions of the second angle from one measured value can be further simplified by dividing the 656.83° by 3 to obtain 218.94°. Thus for methyl chloride, if only the H–C–Cl angle was measured, the H–C–H angle would be 218.94° − 108.0° = 110.9°. The rounded-off value of 219° is apparent in Table 2 by simple addition of ∠H–C–H and its corresponding ∠H–C–X.

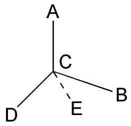

Fig. 1

A geometric procedure for the determination of bond angles for CA_3B may be found in Mislow's monograph[8] and

Table 1 Estimating tetrahedral bond angles

A regular tetrahedron has six spatial angles.
The sum of these spatial angles for a tetrahedron with all four groups the same (CA_4) is 6 × 109.4712206° or 656.827 323 6°. To the nearest degree, that value is 657°.
For a tetrahedron with one group different (CA_3B), there are two different bond angles. The sum of these angles can be approximated to be 219°, one third of 657°.

$$3\angle ACB + 3\angle ACA = 657°$$

This equation simplifies to: $\angle ACB + \angle ACA = 219°$
For a tetrahedron with disubstitution by the same group (CA_2B_2), the approximate sum involves three different angles.

$$\angle ACA + \angle BCB + 4\angle ACB = 657°$$

For a tetrahedron with disubstitution by two different groups (CA_2BD), the approximate sum uses four different angles.

$$\angle ACA + \angle BCD + 2\angle ACD + 2\angle ACB = 657°$$

For a tetrahedron with all groups different (CABDE), the approximate sum comes from six different angles.

$$\angle ACB + \angle ACD + \angle ACE + \angle BCD + \angle BCE + \angle DCE = 657°$$

Table 2 CH_3X bond angles from microwave methods and calculated H–C–H angles (all values in degrees)

X	∠H–C–X	∠H–C–H	Total angles[a]	∠H–C–H[b]	∠H–C–H[c]
F	108.58[5]	110.33[5]	656.73	110.35	110.36
Cl	108.0[7]	110.7[6]	656.1	110.90	110.94
Br	107.23[7]	111.4[6]	655.89	111.62	111.71
I	106.97[7]	111.6[6]	655.71	111.85	111.97

[a] Total angles = 3∠H–C–H + 3∠H–C–X. [b] Calculated from eqn. (1) or (2). [c] Calculated from "total angles" (218.94° − ∠H–C–X).

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Carroll's text[9] wherein the operative equation for methyl chloride is:

$$3 \sin^2 \theta_{\angle \text{H–C–Cl}} = 2(1 - \cos \theta_{\angle \text{H–C–H}}) \qquad (1)$$

Another version of eqn. (1) is:

$$\sqrt{3}/2 \sin \theta_{\angle \text{H–C–Cl}} = \sin 1/2\theta_{\angle \text{H–C–H}} \qquad (2)$$

Eqn. (2) can be derived by dividing both sides of eqn. (1) by four, substituting the cosine term with $\sin^2 1/2\theta_{\angle \text{H–C–H}}$, and taking the square root of both sides. The value $\sqrt{3}/2$ or 0.866 is also the sine of 60° or the cosine of 30°.

A comparison of the two methods is instructive. For the methyl halides when the ∠H–C–X angle is previously determined, the calculated values for ∠H–C–H by each method are also given in Table 2. The differences range from 0.01 to 0.12°.

If there is disubstitution (CA_2B_2) such as with CH_2Cl_2, then three angles have to be considered. With the trigonometric method, the third angle is calculated by means of the equation

$$\cos \theta_{\angle \text{H–C–Cl}} = \cos 1/2\theta_{\angle \text{H–C–H}} \cos 1/2\theta_{\angle \text{Cl–C–Cl}} \qquad (3)$$

For methylene chloride, the Cl–C–Cl angle is 111.78° and that of H–C–H is 112°. When these numbers are used in the cosine expression, the value of the H–C–Cl angle is 108.28°. With the "657" or "total angles" method, the working equation would be

$$\angle \text{H–C–H} + \angle \text{Cl–C–Cl} + 4\angle \text{H–C–Cl} = 656.83° \qquad (4)$$

This affords an angle of 108.26° for H–C–Cl. This method is faster and more convenient since the calculations are made without recourse to trigonometric tables or pocket calculators. Indeed, the calculation for the monosubstituted case that uses a subtraction from 219° can be done without pencil or paper.

To supplement experimental data, bond angles have been calculated with ever-improving computational techniques. A prominent example is Wiberg's conformational studies on halogenocyclohexanes whose centers fall into the CA_2BD category of Table 1.[10] The sums of the angles around the C–X centers, wherein X is F, Cl or Br, range from 656.5 to 656.7°. The sums of the angles around the C3–C4–C5 center vary from 656.7 to 656.9°. As an example, the angles about the equatorial fluorine-bearing carbon of fluorocyclohexane are: 106.3, 110.1, 110.1, 109.1, 109.1 and 111.9° for a sum of 656.6°. Those angles about C4 are: 106.8, 109.3, 109.3, 110.2, 110.2 and 111.0° for a sum of 656.8°. Since the axial and equatorial hydrogens at C4 are not equivalent, the total angles about C4 fit the CA_2BD category.

The tetrahedra need not be carbon compounds. The bond angles of perchloric acid (CA_3B) in the gas phase as determined by electron diffraction are 105.8 for ∠HO–Cl–O and 112.8° for ∠O–Cl–O.[11] Their sum of 218.6° is close to the predicted 218.94°. For $TiCl_2(CH_3)_2$, gas phase electron diffraction results of McGrady and co-workers gave these angles: ∠Cl–Ti–Cl, 117.3; ∠Cl–Ti–CH_3, 108.9; ∠CH_3–Ti–CH_3, 102.8°.[12] The total is 117.3° + 102.8° + 4 × 108.9° = 655.7°. Belyakov and colleagues studied $SiCl_2(CH_3)_2$ and found these bond angles: 107.5 for ∠Cl–Si–Cl, 108.7 for ∠Cl–Si–CH_3 and 114.2° for ∠CH_3–Si–CH_3.[13] The sum of the six angles is 656.5° from 114.2° + 107.5° + 4 × 108.7°. Table 3 lists DFT-optimized angles for oxyhalides of several heavier transition metals.[14] These are examples of the CA_2B_2 type.

In a CA_2BD type molecule with tetravalent phosphorous, Falshaw *et al.* reported X-ray data on the dimeric structure of 1-D-1,2;5,6-di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol, whose monomer is shown in Fig. 2.[15] The sum of the six angles about one phosphorous was 655.4° and that of the second tetravalent phosphorous was 656.2°.

Table 3 Bond angles (in degrees) of some group VIB oxyhalides

MX_2Y_2	∠X–M–X	∠Y–M–Y	∠X–M–Y	Total angles[a]
CrO_2F_2	108.5	110.6	109.4	656.7
CrO_2Cl_2	109.2	110.9	109.2	656.9
MoO_2F_2	106.2	113.2	109.4	657.1
MoO_2Cl_2	106.5	112.6	109.3	656.3
WO_2F_2	106.3	115.7	108.6	656.4
WO_2Cl_2	106.3	114.2	109.0	656.5

[a] Total angles calculated from ∠X–M–X + ∠Y–M–Y + 4∠X–M–Y.

The tetrahedral total angle of 656.83° also holds for centers with four different substituents (CABDE). For the angles at the spiro (C5) junction of (8*RS*,5*SR*,7*SR*)-7-benzoyl-8-hydroxy-8-phenylspiro[4.5]decan-1-one (Fig. 3), Rao and colleagues reported the following: ∠C1–C5–C6, 113.7; ∠C1–C5–C4, 99.8; ∠C6–C5–C4, 113.8; ∠C1–C5–C10, 109; ∠C6–C5–C10, 110.1; ∠C4–C5–C10, 110°.[16] The total of these angles is 656.4°, which is close to 656.83°.

The 657 method could be used for the prediction of a missing value. For example, Fondekar *et al.* reported selected geometric parameters for (1*S*,2*R*)-1-amino-2-methoxycyclohexane-1-carboxamide hydrochloride 0.25 hydrate (Fig. 4).[17] Five angles about C1, a CABDE type, were listed; their sum was 545.70°. The angle C2–C1–C6 was missing. From the difference between 656.83 and 545.70° this value should be 111.13°. The authors have kindly supplied us with the complete CIF file in which the "missing angle" is 111.01(11)°.

For situations remote from the ideal tetrahedron, the total angles method is less helpful for certain CA_3B hydrocarbons. For the case of cubane, if one of the angles is 90° the other angle would be 129° (219° − 90°). The trigonometric value is 125.26°. According to Fleischer's X-ray results, there are three values for the C–C–H bond angles: 123(2), 126(2) and 127(2)°.[18] Thus both values fall within the limits of the data. An extreme situation would be 120°. Here the trigonometric value is 90° and the total angles value is 99°. At such values the tetrahedron's central atom is pushed into the plane of the three A atoms to give a trigonal pyramid. If the central atom

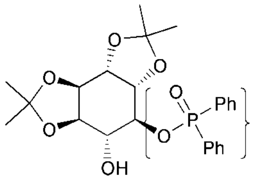

Fig. 2

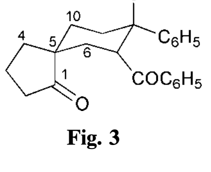

Fig. 3

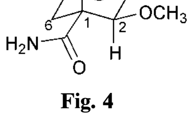

Fig. 4

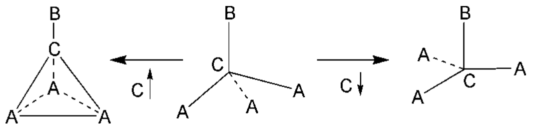

Fig. 5

is pulled away from that plane to an A–C–A angle of 60°, another extreme, the tetrahedrane, is generated. The two processes are shown in Fig. 5. A comparison of the methods over a wide range is shown in Table 4.

These results suggest that the 657 method in its 219 form has value for approximating CA_3B bond angles over the range of most tetrahedral compounds. The extreme bond angles, such as 60, 90 or 120, give rise to structures not normally encountered in organic chemistry.

Table 4 Differences of computational results with CA_3B angles (in degrees)

∠A–C–A	∠A–C–B[a]	∠A–C–B[b]	Δ[c]
60	144.74	158.94	14.20
90	125.26	128.94	3.68
100	117.80	118.94	1.14
105	113.64	113.94	0.30
110	108.94	108.94	0
115	103.13	103.94	0.81
120	90	98.94	8.94

[a] Calculated from eqn. (1) or (2). [b] Calculated by "total angles" (218.94° − ∠A–C–A) . [c] Difference in ∠A–C–B calculated by the two methods.

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