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Average Values of Bond Angles

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A number of definitions with clear physical significance regarding the "average bond angles" (nonlinear case) are presented. Simple expressions of the average angles in terms of the linear and quadratic mean values of the displacements in the internuclear distances are given. The differences in the various average angles for H_2O, D_2O, CH_4, CD_4 and SO_2 are estimated by means of a normal-coordinate analysis. The differences are shown to be small fractions of one degree. The root-mean-square angles for linear molecules (HCN, DCN, CO_2 and CS_2) are also calculated.

In a previous paper,[1] the merits and demerits of the two "average structures" (r_g and r_z) have been discussed. The r_g distance, which represents a thermal-average value of an instantaneous internuclear distance, is readily accessible from an experiment of gas electron diffraction.[2] A scheme has been devised relating the r_g distance to the r_e and r_z distances[3] defined as the distances between the "equilibrium" and "zero-point average" positions of the nuclei, respectively, with reference to a molecule-fixed coordinate system.[4] This scheme provides a theoretical basis of a comparative study of the molecular structures determined from electron-diffraction and spectroscopic data.[1,5,6] The purpose of the present paper is to extend the theory to the specification of bond angles: A similar scheme of conversion among the "average bond angles" based on various definitions is presented, and the orders of magnitude of their mutual differences are estimated.

Definitions of Bond Angles

Bond angles can simply be defined in terms of the r_e and r_z representations, since they are based on

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[1] K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968).

[2] L. S. Bartell, *ibid.*, **23**, 1219 (1955); K. Kuchitsu, This Bulletin, **40**, 498 (1967).

[3] T. Oka, *J. Phys. Soc. Jap.*, **15**, 2274 (1960).

[4] Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, **36**, 1108 (1962).

[5] K. Kuchitsu and S. Konaka, *ibid.*, **45**, 4342 (1966).

[6] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463 (1968).

"nuclear positions." For a set of X—Y and Y—Z bonds in a molecule, the cosine rule can be applied to the bonded and nonbonded (r_e and r_z) distances, r_1(X—Y), r_2(Y—Z) and r_3(X—Z), to make equilibrium and zero-point average bond angles, ϕ_e and ϕ_z respectively,

$$\phi = \cos^{-1}[(r_1^2+r_2^2-r_3^2)/2r_1r_2] \tag{1}$$

An effective bond angle, ϕ_s, corresponding to the r_s coordinates[7] is often used in microwave spectroscopy. However, since no definite physical significance can be attached to the r_s coordinates, one needs to be content with a qualitative estimate[8] that ϕ_s should be very close to ϕ_e.

On the other hand, some consideration is needed in gas electron diffraction to define physically significant bond angles,[9] since only thermal-average internuclear distances, instead of angles or nuclear positions, are measured by this technique.[10] The r_g distance for a nonbonded pair does not correspond exactly to any geometrical arrangement consistent with the corresponding r_g distances for bonded pairs. As is known in terms of the linear and nonlinear shrinkage effect,[11,12] an "effective" bond angle (provisionally named ϕ_G) calculated from the bonded and nonbonded r_g distances by Eq. (1) is, in general, different from the ϕ_e or ϕ_z angles.[13,14] It should also be different from the "thermal-average value of an instantaneous bond angle" (here denoted as ϕ_g) defined in parallel with r_g

$$\phi_g = \langle\cos^{-1}[(r_1^2+r_2^2-r_3^2)/2r_1r_2]\rangle_T \tag{2}$$

where T represents the Boltzmann statistical average for temperature T over all the vibrational states of the molecule.[15] The differences between ϕ_g and ϕ_e for simple hydrides (water,[16,17] ammonia[17-20] and methane[21]), often denoted as $\langle\Delta\alpha\rangle$, have been investigated in detail in relation to the anharmonicity in the angle-bending vibrations and to the hydrogen-deuterium isotope effect.[22]

It may also be useful for some purpose to consider ϕ_c defined by

$$\phi_c \equiv \cos^{-1}\langle\cos\phi\rangle = \cos^{-1}\langle(r_1^2+r_2^2-r_3^2)/2r_1r_2\rangle \tag{3}$$

The angles ϕ_α and $\phi_\alpha{}^0$ corresponding to the r_α and $r_\alpha{}^0$ structures,[4] which may be derived from electron-diffraction experiments, have been used in some previous studies;[1,6,23] ϕ_α is supposed to be essentially the angle composed of the thermal-average nuclear positions, so that $\phi_\alpha{}^0$, the angle extrapolated to 0°K, should be essentially equivalent to ϕ_z. For PF_3,[24] the $\phi_\alpha{}^0$ angle was estimated to be nearly equal to the ϕ_α within the experimental uncertainty of 0.2°.

Analytical Expressions

Nonlinear Case. For a nonlinear arrangement ($\phi_e<\pi$), Eq. (1) may be expanded in terms of the instantaneous displacements in the internuclear distances around ϕ_e,

$$\Delta r_i \equiv r_i - (r_e)_i \qquad (i=1,2,3) \tag{4}$$

$$\phi = \phi_e + \sum_{i=1}^{3} a_i\Delta r_i + \sum_{\substack{i=1\\ i\leq j}}^{3}\sum_{j=1}^{3} b_{ij}\Delta r_i\Delta r_j + \cdots \tag{5}$$

The coefficients a and b are functions of ϕ_e and $\sigma_i \equiv (r_e)_i{}^{-1}$,

$$\begin{aligned}
a_k &= \sigma_k \cot\phi_e - \sigma_l \operatorname{cosec}\phi_e\\
a_3 &= (\sigma_1\sigma_2/\sigma_3)\operatorname{cosec}\phi_e\\
b_{kk} &= \frac{1}{2}\sigma_1\sigma_2\operatorname{cosec}\phi_e - \left(\sigma_k{}^2+\frac{1}{2}a_k{}^2\right)\cot\phi_e\\
b_{12} &= (\sigma_1{}^2+\sigma_2{}^2)\operatorname{cosec}\phi_e - (\sigma_1\sigma_2+a_1a_2)\cot\phi_e\\
b_{k3} &= (\sigma_1\sigma_2/\sigma_3)a_l \operatorname{cosec}^2\phi_e\\
b_{33} &= \frac{1}{2}(\sigma_1\sigma_2\operatorname{cosec}\phi_e - a_3{}^2\cot\phi_e)
\end{aligned} \tag{6}$$

where $k=1$, 2 and $l=2$, 1 are to be taken in the same order. According to a simple order-estimation, higher-order terms of Eq. (5) do not contribute significantly to the following discussions.

By taking the thermal average of ϕ in Eq. (5), one gets a simple analytical expression of ϕ_g,

$$\phi_g = \phi_e + \sum_i a_i\langle\Delta r_i\rangle + \sum\sum_{i\leq j} b_{ij}\langle\Delta r_i\Delta r_j\rangle + \cdots \tag{7}$$

Since $(r_g)_i$ is defined as $\langle r_i\rangle$, ϕ_G defined above is given by

$$\phi_G = \cos^{-1}[(\langle r_1\rangle^2 + \langle r_2\rangle^2 - \langle r_3\rangle^2)/2\langle r_1\rangle\langle r_2\rangle] \tag{8}$$

so that it may be related to ϕ_g as

$$\phi_G = \phi_g - \sum\sum_{i\leq j} b_{ij}(\langle\Delta r_i\Delta r_j\rangle - \langle\Delta r_i\rangle\langle\Delta r_j\rangle) + \cdots \tag{9}$$

In a similar way, it follows from Eq. (3) that

$$\phi_c = \phi_g + \frac{1}{2}\cot\phi_e\sum_{i=1}^{3}\sum_{j=1}^{3} a_ia_j(\langle\Delta r_i\Delta r_j\rangle - \langle\Delta r_i\rangle\langle\Delta r_j\rangle) + \cdots \tag{10}$$

If ϕ is expanded around the zero-point average nuclear positions, instead of the equilibrium positions as is shown in Eq. (4), ϕ_g can be related to ϕ_z as

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[7] C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958); *Trans. Amer. Crystallogr. Soc.*, **2**, 157 (1966).

[8] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **4**, 41 (1969).

[9] K. Kuchitsu, This Bulletin, **32**, 748 (1959).

[10] In most of the past electron-diffraction studies, an effective bond angle derived from Eq. (1) with bonded and nonbonded r_a distances[2] are reported without specification.

[11] Y. Morino, J. Nakamura, and P. W. Moore, *J. Chem. Phys.*, **36**, 1050 (1962).

[12] Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, *ibid.*, **36**, 1109 (1962).

[13] L. S. Bartell and D. A. Kohl, *ibid.*, **39**, 3097 (1963).

[14] Bartell and Kohl,[13] in their analysis of hydrocarbon structures, introduced a "mean" structure with a set of the r_G parameters, which consist of r_g bond distances and ϕ_G angles. They further estimated the shrinkages in the nonbonded r_G distances dependent on the torsional motions of the hydrocarbon chain as functions of the mean-square librational amplitudes.

[15] For simplicity, the subscript T will be left out from the subsequent expressions.

[16] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962).

[17] L. S. Bartell, *ibid.*, **38**, 1827 (1963).

[18] E. A. Halevi, *Trans. Faraday Soc.*, **54**, 1441 (1958).

[19] Y. Morino, K. Kuchitsu, and S. Yamamoto, *Spectrochim. Acta*, **24A**, 335 (1968).

[20] K. Kuchitsu, J. P. Guillory, and L. S. Bartell, *J. Chem. Phys.*, **49**, 2488 (1968).

[21] K. Kuchitsu and L. S. Bartell, *ibid.*, **36**, 2470 (1962).

[22] M. Wolfsberg, *Ann. Rev. Phys. Chem.*, **20**, 449 (1969).

[23] K. Kuchitsu, *J. Chem. Phys.*, **44**, 906 (1966).

[24] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

TABLE 1. AVERAGE VALUES OF DISPLACEMENTS[a)]

	$\langle \Delta r_1 \rangle$	$\langle \Delta r_3 \rangle$	$\langle \Delta z_1 \rangle_0$	$\langle \Delta z_3 \rangle_0$	$\langle \Delta r_1^2 \rangle$	$\langle \Delta r_3^2 \rangle$	$\langle \Delta r_1 \Delta r_2 \rangle$	$\langle \Delta r_1 \Delta r_3 \rangle$	Ref.[b)]
H_2O	1713	2350	1431	2255	465	1282	10	334	16, 28
D_2O	1271	1649	1061	1587	337	913	3	231	
CH_4	2159	2810	1405	2294	618	1556	17	452	21
CD_4	1594	2048	1029	1681	446	1093	2	312	
SO_2	477	762	408	757	124	302	−10	80	29
HCN[c)]	1688	618	−431	25	570	601	−14	508	30
DCN[c)]	1250	395	−122	232	407	448	−21	357	
CO_2	503	471	235	471	121	156	−39	79	31
CS_2	448	196	98	196	151	170	−63	84	32

	$\langle \Delta r_2 \rangle$	$\langle \Delta z_2 \rangle_0$	$\langle \Delta r_2^2 \rangle$	$\langle \Delta r_2 \Delta r_3 \rangle$	Ref.
HCN[c)]	538	456	117	96	30
DCN[c)]	515	354	117	89	

a) See text for notations: in 10^{-5} Å for the linear averages and 10^{-5} Å^2 for the quadratic averages.
b) References from which the potential constants were taken. See also Ref. 27.
c) The numbers 1 and 2 represent the C–H and C≡N bonds, respectively. They are equivalent for the other molecules.

$$\phi_g = \phi_z + \sum_i a_i \langle r_i - (r_z)_i \rangle + \sum_{i \leq j}\sum b_{ij} \langle [r_i - (r_z)_i][r_j - (r_z)_j] \rangle + \cdots \qquad (11)$$

which may be rewritten as

$$\phi_g = \phi_z + \sum_i a_i [(r_g)_i - (r_z)_i] + \sum_{i \leq j}\sum b_{ij} (\langle \Delta r_i \Delta r_j \rangle_T + \langle \Delta z_i \rangle_0 \langle \Delta z_j \rangle_0 - \langle \Delta r_i \rangle_T \langle \Delta z_j \rangle_0 - \langle \Delta r_j \rangle_T \langle \Delta z_i \rangle_0) + \cdots \qquad (12)$$

by noting that $\phi_e \simeq \phi_z$ and that[4)] $r_z \simeq r_e + \langle \Delta z \rangle_0$, where Δz is the projection of Δr onto the z axis taken in the direction of the equilibrium nuclear positions of the pair, and the average 0 is taken for the ground vibrational state.

Linear Case. For a linear arrangement, where ϕ_e tends to π, Eq. (5) is no longer valid. Although it is not impossible to define ϕ_g in a similar way to Eq. (2) providing that $\phi \leq \pi$, the arccosine function in Eq. (2) can not readily be expanded in terms of the displacements around $\phi = \pi$, so that the problem deviates from that of the ordinary normal-coordinate analysis. It is much simpler, instead, to take the mean-square angle, $\langle (\pi - \phi)^2 \rangle$, as a measure of the average bending displacement. It can be shown that

$$\langle (\pi - \phi)^2 \rangle = \sum_i c_i \langle \Delta r_i \rangle + \sum_{i \leq j}\sum d_{ij} \langle \Delta r_i \Delta r_j \rangle + \cdots \qquad (13)$$

where

$$c_k = 2(\sigma_1 + \sigma_2) = -c_3, \quad d_{kk} = -\sigma_k(2\sigma_k + \sigma_l),$$
$$d_{12} = -2(\sigma_1^2 + \sigma_1\sigma_2 + \sigma_2^2), \quad d_{k3} = 2\sigma_k(\sigma_1 + \sigma_2), \qquad (14)$$
$$d_{33} = -\sigma_1\sigma_2$$

The first sum may be rewritten as

$$\sum_i c_i \langle \Delta r_i \rangle = 2(\sigma_1 + \sigma_2)\delta_g \qquad (15)$$

where δ_g is the "linear shrinkage" defined by[11)]

$$\delta_g = (r_g)_1 + (r_g)_2 - (r_g)_3 \qquad (16)$$

One may also define ϕ_c given in Eq. (10) and another effective average angle ϕ_ρ,

$$\phi_\rho = \pi - [\langle \Delta \rho_1^2 \rangle^{1/2}/(r_e)_1 + \langle \Delta \rho_2^2 \rangle^{1/2}/(r_e)_2] \qquad (17)$$

where $\Delta \rho_i$ represents a displacement perpendicular to the equilibrium molecular axis.

Application

The average displacements in the above equations can be calculated by means of a normal-coordinate analysis[16–21,25–27)] provided the quadratic and higher-order potential constants for the molecule are known. Thus the present problem is, in principle, straightforward.

Table 1 lists the average displacements for a number of simple hydrides (with their full deuterides) and nonhydrides calculated by the use of the experimental anharmonic potential constants given in the literature.[28–35)] It should be noted that the cross mean values of bonded and nonbonded displacements, $\langle \Delta r_1 \Delta r_3 \rangle$ and $\langle \Delta r_2 \Delta r_3 \rangle$, are comparable in the order of magnitude with the corresponding mean-square displacements, $\langle \Delta r_1^2 \rangle$, $\langle \Delta r_2^2 \rangle$ and $\langle \Delta r_3^2 \rangle$.

The differences among the various angles calculated for nonlinear molecules are given in Table 2, together with their experimental ϕ_e.[28,36)] The differences between the ϕ_g and ϕ_e for H_2O (D_2O) and CH_4 (CD_4) are essentially equal to their equivalents, $\langle \Delta\alpha \rangle$, re-

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25) A. Reitan, *Acta Chem. Scand.*, **12**, 785 (1958); Thesis (Trondheim, Norway) (1958).

26) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

27) K. Kuchitsu, *ibid.*, **40**, 505 (1967).

28) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956).

29) Y. Morino, Y. Kikuchi, S. Saito, and E. Hirota, *J. Mol. Spectrosc.*, **13**, 95 (1964).

30) T. Nakagawa and Y. Morino, This Bulletin, **42**, 2212 (1969).

31) C. P. Courtoy, *Can. J. Phys.*, **35**, 608 (1957).

32) B. P. Stoicheff, *ibid.*, **36**, 218 (1958).

33) K. Kuchitsu and Y. Morino, This Bulletin, **38**, 805, 814 (1965).

34) S. J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes," Universitetsforlaget, Oslo, and Elsevier, Amsterdam (1968), pp. 202, 311.

35) A part of the entries have already been published by the present author (Table 1 of Ref. 27). See Refs. 16, 21, 25, 26, and 34 for earlier calculations of the mean displacements. The mean-square amplitudes and shrinkages for HCN and DCN are in essential agreement with those calculated by Cyvin[34)] by a harmonic approximation.

36) S. Saito, *J. Mol. Spectrosc.*, **30**, 1 (1969).

Table 2. Differences in average angles (Nonlinear Case) (in degrees)

	ϕ_e	$\phi_g-\phi_e$	$\phi_g-\phi_G$	$\phi_g-\phi_c$	$\phi_g-\phi_z$	$\phi_z-\phi_e$ c)
H_2O	104.523 a)	0.022	0.367	0.176	0.025	−0.07 d)
D_2O	104.474 a)	−0.069	0.280	0.131	0.017	−0.12 d)
CH_4	109.471	−0.286	0.360	0.218	−0.295	0
CD_4	109.471	−0.228	0.286	0.164	−0.241	0
SO_2	119.33_0 b)	0.043	0.091	0.061	0.034	0.02_2 b)

a) Ref. 28.
b) Ref. 29 and 36.
c) Experimental estimates.
d) Refs. 19 and 23.

ported in previous studies.[16,21] In addition, the differences between the $\phi_g-\phi_e$ and $\phi_g-\phi_z$ calculated here are consistent with the corresponding experimental estimates of $\phi_z-\phi_e$ derived from the rotational constants by way of a slightly different procedure.[3,37] As is expected from the previous estimates of nonlinear shrinkages,[12,38] the differences among the various angles are as small as a few tenths of a degree, which are comparable with or smaller than ordinary experimental uncertainties. Nevertheless, it may not always be permissible to simply ignore the differences without discretion. The differences may be significantly larger when the molecule has a low-frequency, large-amplitude bending vibrations. This remark applies particularly to the dihedral angles of torsion[13] and the angles associated with ring-puckering motions, to which the above-mentioned definitions of the average angles can be extended.

Table 3. Average angles (Linear Case) (in degrees)

	$\langle(\pi-\phi)^2\rangle^{1/2}$	$\pi-\phi_c$ a)	$\pi-\phi_p$ b)
HCN	13.643	13.675	13.894
DCN	12.624	12.650	12.785
CO_2	7.747	7.753	7.786
CS_2	7.673	7.679	7.700

a) Equation (3) is applied on condition that $\phi\leqq\pi$.
b) Equation (17).

The root-mean-square angles for linear molecules are listed in Table 3. The differences among them seem to be smaller than the uncertainties in their estimates.

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37) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **37**, 1668 (1962).

38) Ref. 34, p. 319ff.