# The Molecular Structures of Dimethyl-, Diethyl- and Dipropylzinc Determined by Gas Phase Electron Diffraction. Normal Coordinate Analysis and *ab initio* Molecular Orbital Calculations on Dimethylzinc

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Dimethyl-, diethyl- and dipropylzinc (Me_2Zn Et_2Zn and n-Pr_2Zn) have been investigated by gas phase electron diffraction. The Zn − C bond distance in Me_2Zn, 193.0(2) pm, is significantly smaller than in Et_2Zn and n-Pr_2Zn, 195.0(2) and 195.2(3) pm, respectively. The valence angle <ZnCC is 114.5(3)° in Et_2Zn and 114.5(5)° in n-Pr_2Zn. 74(4) % of the alkyl chains in n-Pr_2Zn are in a *synclinal* conformation suggesting the presence of a weak attraction between the Zn atom and the terminal methyl group. Least squares refinement of a relatively simple valence force field for Me_2Zn yielded force constants that reproduce the frequencies of the normal modes according to the latest assignment to the nearest cm^{-1}. The structure of Me_2Zn has been fully optimized by *ab initio* molecular orbital calculations with a *double zeta* basis. The optimal structure is in reasonable agreement with the experimental results, and the orbital energy sequence in agreement with the published PE spectrum. Population analysis indicates that the $3d$ electrons of Zn must be regarded as non-bonding and the Zn − C bond as a pure σ-bond.

When di-5-hexenylzinc is prepared from di-5-hexenylmercury by metal exchange: [CH_2 =CH-$(CH_2)_4]_2Hg + Zn \rightarrow [CH_2 = CH(CH_2)_4]_2Zn + Hg$, di-(cyclopentylmethyl)zinc is obtained as a biproduct.[1] If the reaction mixture is kept at 120 °C for 3½ days, di(cyclopentylmethyl)zinc is formed in approximately 90 % yield.[1] The cyclization reaction is thought to proceed through a four-center transition state:
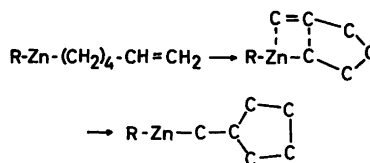
Di-4-pentenylzinc is found to be stable under the same conditions, probably because an analogous cyclization reaction would yield a strained cyclobutane ring.[1] The proton NMR spectrum of this compound shows an anomalous downfield shift of one of the vinyl H atoms relative to the parent hydrocarbon. This shift has been interpreted as evidence for weak intramolecular interaction between the metal atom and the double bonds.[1]

Recently we have investigated di-4-pentenylzinc by gas phase electron diffraction. The scattering pattern was found to be consistent with a molecular model in which both chains are coiled back to bring the CC double bonds close to the Zn atom, Zn − C ~ 220 pm.[2] In the hope that information about bond distances, valence angles, force fields and conformational preferences of simple dialkylzinc compounds would put this study on a firmer basis, we decided to investigate dimethylzinc, Me_2Zn, diethylzinc, Et_2Zn and dipropylzinc, n-Pr_2Zn.

Several studies of the vibrational spectrum of Me_2Zn have made it clear that the valence angle ∠CZnC is 180° and that the barrier to internal rotation is negligible.[3,4] The instantaneous sym-

metry of the molecule is thus D_3. The moment of inertia obtained by rotational Raman spectroscopy yields a $Zn-C$ bond distance of 192.9(4) pm.[5]

Normal coordinate analysis and calculation of spectroscopic parameters. Me_2Zn. Since the methyl groups undergo virtually free internal rotation, a classification of the normal modes must be made using the permutation – inversion double group G_{36}^+ introduced by Hougen.[6] Moreover, the conventional *FG* formalism for rigid molecules is no longer appropriate, and an extension for dealing with molecules exhibiting nearly free internal rotation has been presented by Bunker.[7] Symmetry coordinates are chosen that render the *G* matrix rigorously independent of the torsional angle, the *F* matrix dependence is then expected to be small. Furthermore, the vibrational and torsional modes can be separated provided the torsional frequency is so low that the torsional angle remains essentially constant during the period of a genuine vibration. Proceeding as usual it is then possible to calculate 3N-7 normal coordinates and frequencies for some fixed value of the torsional angle. The resulting force field may be considered to be a reasonable approximation to the true, torsional dependent field.

The vibrational spectra of gaseous, liquid and solid Me_2Zn have recently been reinvestigated and partly reassigned by Butler and Newbury,[4] see Table 1. Using their results we have carried out a least squares refinement of the molecular force field for an eclipsed (D_{3h}) conformation employing

a program written by G. O. Sørensen[8] and modified in our laboratory. The symmetry coordinates are listed in Table 2 and correspond to those given for dimethylacetylene[7] ($\gamma = 0°$). Δr, ΔR, $\Delta\alpha$, $\Delta\beta$, $\Delta\phi$ refer to small displacements in the $C-H$, $Zn-C$ bond lengths and $\angle HCH$, $\angle ZnCH$, $\angle CZnC$ bond angles, respectively.

In order to keep the force field as simple as possible we first assumed a diagonal valence force field. It was found, however, that a satisfactory agreement required the inclusion of the interaction constants $f_{R\beta}$, and f_{rr} (within the methyl groups) and $f'_{\alpha\alpha}$ and $f'_{\beta\beta}$ (between the methyl groups). The last two small interactions will presumably show a strong torsional dependence, they are however essential for splitting of the otherwise nearly degenerate modes v_9/v_{13} and v_{10}/v_{14}. The final force field is listed in Table 3, and in Table 1 we list the calculated frequencies and the potential energy distributions for each mode. The agreement between this and earlier[9] force fields is reasonable.

Following Bunker and Hougen[10] we have calculated the torsional dependence of degenerate modes for several plausible force fields. Bunker and Hougen have shown that for dimethylacetylene close-lying pairs of modes can be either (E_{1d}, E_{2d}) or (E_{1s}, E_{2s}) depending on the γ-dependent terms in the force field. For Me_2Zn the situation is more clear-cut in that two of these pairs (v_9, v_{13}) and (v_{10}, v_{14}) are not found to be nearly degenerate. Force constants of type (6) in Bunker and Hougen's

Table 1. Observed and calculated frequencies for Me_2Zn (cm^{-1}).

Vibration number	Symmetry species	Obs. frequency[a]	Calc. frequency	Potential energy distribution
v_1	a_{1s}	2916	2915	99r
v_2	a_{1s}	1180	1180	$73\alpha + 36\beta$
v_3	a_{1s}	511	510	114R
$v_5{}^b$	a_{4s}	2914	2915	99r
v_6	a_{4s}	1183	1183	$72\alpha + 35\beta$
v_7	a_{4s}	613	613	114R
v_8	e_{1d}/e_{1s}	2970	2970	99r
v_9	e_{1d}/e_{1s}	1301	1301	96α
v_{10}	e_{1d}/e_{1s}	704	704	95β
v_{11}	e_{1d}	157^c	157	98ϕ
v_{12}	e_{2d}/e_{2s}	2970^c	2970	99r
v_{13}	e_{2d}/e_{2s}	1435^c	1435	97α
v_{14}	e_{2d}/e_{2s}	611	611	98β

[a] Ref. 4. [b] Assuming free rotation of methyl groups, there is no methyl torsional mode. [c] These modes have not been observed in the gas phase. v_{11} and v_{13} are transferred from corresponding liquid data, v_{12} is set equal to v_8 gas phase frequency.

Table 2. Symmetry coordinates for Me_2Zn in eclipsed conformation.[a]

$a_{1s}(a_1')$

$$s_1 = \frac{1}{\sqrt{6}} (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6)$$

$$s_2 = \frac{1}{\sqrt{6}} (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6)$$

$$s_3 = \frac{1}{\sqrt{6}} (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6)$$

$$s_4 = \frac{1}{\sqrt{2}} (\Delta R_1 + \Delta R_2)$$

$a_{4s}(a_2'')$

$$s_5 = \frac{1}{\sqrt{6}} (\Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4 - \Delta r_5 - \Delta r_6)$$

$$s_6 = \frac{1}{\sqrt{6}} (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6)$$

$$s_7 = \frac{1}{\sqrt{6}} (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)$$

$$s_8 = \frac{1}{\sqrt{2}} (\Delta R_1 - \Delta R_2)$$

$e_{1d}(e')$

$$s_{9a} = \frac{1}{\sqrt{12}} (2\Delta r_1 - \Delta r_2 - \Delta r_3 + 2\Delta r_4 - \Delta r_5 - \Delta r_6)$$

$$s_{9b} = \frac{1}{2} (\Delta r_2 - \Delta r_3 + \Delta r_5 - \Delta r_6)$$

$$s_{10a} = \frac{1}{\sqrt{12}} (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 + 2\Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6)$$

$$s_{10b} = \frac{1}{2} (\Delta\alpha_2 - \Delta\alpha_3 + \Delta\alpha_5 - \Delta\alpha_6)$$

$$s_{11a} = \frac{1}{\sqrt{12}} (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + 2\Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6)$$

$$s_{11b} = \frac{1}{2} (\Delta\beta_2 - \Delta\beta_3 + \Delta\beta_5 - \Delta\beta_6)$$

$$s_{12a} = \Delta\phi_x$$

$$s_{12b} = \Delta\phi_y$$

$e_{2d}(e'')$

$$s_{13a} = \frac{1}{2} (\Delta r_2 - \Delta r_3 - \Delta r_5 + \Delta r_6)$$

$$s_{13b} = \frac{1}{\sqrt{12}} (2\Delta r_1 - \Delta r_2 - \Delta r_3 - 2\Delta r_4 + \Delta r_5 + \Delta r_6)$$

$$s_{14a} = \frac{1}{2} (\Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_5 + \Delta\alpha_6)$$

$$s_{14b} = \frac{1}{\sqrt{12}} (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 - 2\Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6)$$

$$s_{15a} = \frac{1}{2} (\Delta\beta_2 - \Delta\beta_3 - \Delta\beta_5 + \Delta\beta_6)$$

$$s_{15b} = \frac{1}{\sqrt{12}} (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - 2\Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6)$$

[a] Redundancies are removed by the program. Hydrogen atoms 1/4, 2/5 and 3/6 are eclipsed.

Table 3. F matrix and force constants for Me_2Zn.

a_{1s}		a_{4s}	
$F_{11}=f_r+2f_{rr}$		$F_{55}=f_r+2f_{rr}$	
$F_{22}=f_\alpha$		$F_{66}=f_\alpha$	
$F_{33}=f_\beta$		$F_{77}=f_\beta$	
$F_{34}=\sqrt{3}\,f_{R\beta}$		$F_{78}=\sqrt{3}\,f_{R\beta}$	
$F_{44}=f_R$		$R_{88}=f_R$	

e_{1d}		e_{2d}	
$F_{99}=f_r-f_{rr}$		$F_{1313}=f_r-f_{rr}$	
$F_{1010}=f_\alpha+f'_{\alpha\alpha}$		$F_{1414}=f_\alpha-f'_{\alpha\alpha}$	
$F_{1111}=f_\beta+f'_{\beta\beta}$		$F_{1515}=f_\beta-f'_{\beta\beta}$	
$F_{1212}=f_\phi$			

f_r	476.4 N/m	f_α	0.517 aJ/rad^2
f_R	241 N/m	f_β	0.3057 aJ/rad^2
f_{rr}	4.9 N/m	f_ϕ	0.322 aJ/rad^2
		$f'_{\alpha\alpha}$	-0.054 aJ/rad^2
$f_{R\beta}$	3.20 nN/rad	$f'_{\beta\beta}$	0.0412 aJ/rad^2

paper are thus excluded in these cases, giving modes of species (E_{1s}, E_{2s}). For the close-lying pair (v_8, v_{12}) both fields (6) and (7) are plausible. However, due to lower degenerate modes this gives (E_{1s}, E_{2s}) in either case. It is important to realize that these arguments hold only if we assume that cos 6γ-terms predominate over cos 12γ- (and higher) terms — which seems physically reasonable. We thus arrive at the conclusion that (E_{1s}, E_{2s}) seems more probable than (E_{1d}, E_{2d}) for all modes except skeletal bending, contrary to what has previously been tacitly assumed by others.[4,11]

Root mean square vibrational amplitudes, l, and perpendicular amplitude correction coefficients, K, were calculated using the force constants given in Table 3.

Et$_2$Zn and n-Pr$_2$Zn. Approximate force fields for these molecules (Table 4) were constructed from the force field of Me_2Zn and the valence force constants of saturated alkanes.[12] The C—C stretching force constant of Et_2Zn was adjusted to reproduce the observed frequency at 922 cm^{-1}.[13] The value adopted for the ZnCC bending force constant yields bending frequencies around 270 cm^{-1}, in agreement with a recent normal coordinate calculation.[14] For torsional force constants we have used values estimated for 1-chloropropane.[15] Though reasonable, these values must be regarded as very uncertain. Calculations of vibrational amplitudes and correction coefficients were carried out with a program written by Hilderbrandt.[16]

Finally we calculated the vibrational partition functions (defined equal to unity at 0 Kelvin) for two conformers of n-Pr$_2$Zn: One with both chains

Table 4. Approximate valence force fields of Et_2Zn and $n\text{-}Pr_2Zn$.

Stretch (N/m)			
ZnC	242	C(1)H	455
C(1)C(2)	354	C(2)H	470[a]/455[b]
C(2)C(3)	439	C(3)H	470

Bend (aJ/rad^2)			
ZnCC	0.70	C(2)C(3)H	0.645
ZnCH	0.307	HC(1)H	0.550
CCC	1.13	HC(2)H	0.540[a]/0.550[b]
C(2)C(1)H	0.656	HC(3)H	0.540
C(1)C(2)H	0.645[a]/0.656[b]		

Torsion (aJ/rad^2)			
C(1)−C(2)	0.086[a]	C(1)−C(1′)	0.01[b]
C(1)−C(2) (sc)	0.20[b]	C(2)−C(3)	0.086[b]
C(1)−C(2) (ap)	0.14[b]		

Linear bend (aJ/rad^2)			
CZnC	0.322		

Stretch-stretch (N/m)			
ZnC/CC	10	CC/CC	10
C(2)H/C(2)H	4.3[a]/0.0[b]	C(3)H/C(3)H	4.3

Stretch-bend (nN/rad)			
ZnC/ZnCC	4.2	CC/CCH	3.3
ZnC/ZnCH	3.2	CC/CCC	4.2[b]

Bend-bend (aJ/rad^2)			
C(i)C(j)H/C(j)C(i)H(ap)	0.127		

[a] Et_2Zn. [b] $n\text{-}Pr_2Zn$.

in the *antiperiplanar* conformation and one with both chains in a *synclinal* conformation. (For a more accurate description, see the section on electron diffraction.) We regard the square roots of these partition functions as the partition functions of a chain in the *ap* and *sc* conformations, respectively. The ratio $Q_{ap}/Q_{sc} = 1.25$ is greater than unity largely because the torsional force constant is assumed lower in the *ap* conformation.

Molecular orbital calculations. The molecular structure of Me_2Zn was fully optimized by *ab initio* molecular orbital calculations assuming D_{3h} (eclipsed) molecular symmetry. The optimization was carried out by Pulay's force relaxation method[17] using the program MOLFORCE written by S. Sæbø,[18] which is based on MOLECULE written by J. Almlöf.[19]

The basis consisted of four GTO s-functions on H contracted to $2s$[20] and $(7s, 3p)$ functions for C contracted to $\langle 4s, 2p\rangle$.[21] For Zn we chose the $(12s\ 6p\ 4d)$ basis of Roos et al.[22] augmented by two sets of diffuse $4p$ functions, contracted to $\langle 8s\ 6p\ 2d\rangle$. The total energy for the optimized model was -1856.09045 au.

ELECTRON DIFFRACTION

Experimental. The samples of Me_2Zn and Et_2Zn were gifts from J. Weidlein, Stuttgart, and the sample of $n\text{-}Pr_2Zn$ from H. Lehmkuhl, Mülheim.

The electron scattering patterns were recorded on the Oslo electron diffraction unit[23] with nozzle temperatures of about 20 °C (Me_2Zn), 30 °C (Et_2Zn) and 60 °C ($n\text{-}Pr_2Zn$). Exposures were made with

nozzle-to-plate distances of about 48 and 20 cm for Me$_2$Zn, and 48 and 26 cm for Et$_2$Zn and n-Pr$_2$Zn. This study is based on two sets of six plates for Me$_2$Zn, six 48 cm and five 26 cm plates for Et$_2$Zn, and six 48 cm and three 26 cm plates for n-Pr$_2$Zn.

The data were processed by standard methods.[24] The complex atomic scattering factors, f'(s), were calculated from an analytical representation of the atomic potential[25] using a program written by Yates.[26] The molecular intensities were modified through multiplication with $s/|f'_C||f'_{Zn}|$. The average modified molecular intensities covered the ranges:

Me$_2$Zn: $s = 13.75$ to 180.00 nm^{-1} with
$\Delta s = 1.25$ nm^{-1}
and $s = 75.00$ to 325.00 nm^{-1} with
$\Delta s = 2.50$ nm^{-1}
Et$_2$Zn: $s = 20.00$ to 197.50 nm^{-1} with
$\Delta s = 1.25$ nm^{-1}
and $s = 65.00$ to 340.00 nm^{-1} with
$\Delta s = 2.50$ nm^{-1}.
n-Pr$_2$Zn: $s = 40.00$ to 185.00 nm^{-1} with
$\Delta s = 1.25$ nm^{-1}
and $s = 55.00$ to 270.00 nm^{-1} with
$\Delta s = 2.50$ nm^{-1}.

Structure refinement. In accordance with results of spectroscopic studies Me$_2$Zn was assumed to have D_3 symmetry with freely rotating (V=0) methyl groups. The molecular structure is then determined by the Zn$-$C and C$-$H bond distances and the valence angle $\angle$ZnCH.

It was likewise assumed that $\angle$CZnC$= 180°$ in both Et$_2$Zn and n-Pr$_2$Zn.

A molecular model of n-Pr$_2$Zn showing the numbering of the C atoms is shown in Fig. 1. A similar numbering scheme was adopted for Me$_2$Zn and Et$_2$Zn. Hence C(1) refers to the C$_\alpha$ atom in each of the three compounds, C(2) to the C$_\beta$ and C(3) to the C$_\gamma$ atom. The carbon atoms in the other chain are denoted C(1'), C(2') and C(3'), respectively. The H atoms are numbered as the C atom to which they are bonded.
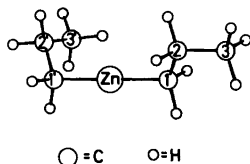

$\bigcirc = C$ $\circ = H$

Fig. 1. Molecular model of n-Pr$_2$Zn. The right hand propyl chain is in the *antiperiplanar* *(ap)* conformation, the left hand chain in a *synclinal (sc)* conformation.

Initial refinements on Et$_2$Zn were carried out assuming a model of C_2 symmetry. It was further assumed that the C$-$CH$_3$ fragments have C_{3v} symmetry and that the methyl groups are oriented in such a way that one C(2)$-$H bond is *anti* the Zn$-$C(1) bond. The $\angle$HC(1)H angle of the methylene group was assumed equal to 106° and to be bisected by the ZnC(1)C(2) plane. Finally all C$-$H bond distances were assumed equal. The molecular structure is then determined by the Zn$-$C, C$-$C and C$-$H bond distances, by the valence angles $\angle$ZnCC, $\angle$ZnCH and $\angle$C(1)C(2)H and by the angle between the planes ZnC(1)C(2) and ZnC(1')C(2'), ϕ[C(1)C(1')]. The final refinements were carried out on a dynamic model with $V(\phi) = \frac{1}{2}V_0 \cos \phi$. ϕ was defined as zero when C(2) and C(2') are eclipsed. The refinement yielded $V_0 = -1.5(16)$ kJ mol^{-1}, *i.e.* a value close to and not significantly different from zero. Introduction of the dynamic model yielded a slight improvement of the fit.

n-Pr$_2$Zn is present in the gas jet as a conformational mixture: The experimental radial distribution curve contains both a peak at about 440 pm corresponding to an *antiperiplanar* *(ap)* Zn$-$C(3) distance, and a shoulder at about 335 pm corresponding to a *synclinal (sc)* distance. Since conformation-dependent distances between atoms in different chains are greater than 475 pm and the experimental radial distribution curves show no perceptible structure in this range, we believe that for our purpose each chain may be regarded as independent of the other. We therefore assumed the mixture to consist of only two conformers, one with both chains in the *ap* conformation, and one with both chains in the *sc* conformation. Both conformers were assumed to have C_2 symmetry. The possible presence of other conformers, as for instance one containing one *ap* and one *sc* chain or one containing two *sc* chains but with molecular symmetry other than C_2, was thus disregarded.

The dihedral angle ϕ[C(1)C(1')] was assumed equal in the two conformers, and was refined as an independent parameter. The resulting value, $\phi = 77(25)°$, appears a reasonable average value for the permissible range, 0 to 180°.

In addition to the assumptions regarding molecular structure which had been made for Et$_2$Zn, it was assumed that the bond distances C(1)$-$C(2) and C(2)$-$C(3) are equal, and that the fragment C(1)$-$C(2)H$_2-$C(3) has C_{2v} symmetry with $\angle$HC(2)H$= 106°$. The valence angle $\angle$C(2)C(3)H was fixed at 110°.

The molecular structure of n-Pr$_2$Zn is then determined by eight independent parameters, the Zn$-$C, C$-$C and C$-$H bond distances, valence angles $\angle$ZnCC, $\angle$ZnCH and $\angle$CCC, and by the mol fraction, χ_{sc} and dihedral angle ϕ(C(1)C(2)) of the *sc* conformer.

Table 5. Bond distances (r_a) and valence angles of Me_2Zn, Et_2Zn and $n-Pr_2Zn$. Dihedral angle (ϕ_{sc}) and mol fraction (χ_{sc}) of *synclinal* chains in $n-Pr_2Zn$. Estimated standard deviations in parentheses in units of the last digit.

	Me_2Zn	Et_2Zn	$n-Pr_2Zn$
Bond distances (pm)			
$Zn-C$	193.0(2)	195.0(2)	195.2(3)
$C-C$		154.0(3)	153.5(5)[a]
$C-H$	110.0(5)	110.5(4)[a]	109.7(4)[a]
Valence angles (deg)			
$\angle ZnCH$	112.5(5)	107.9(8)	106.3(20)
$\angle ZnCC$		114.5(3)	114.5(5)
$\angle CCH$		114.0(13)[b]	[110][c]
$\angle CCC$			113.6(16)
$\phi(C(1)-C(2))_{sc}$ (deg)			60(4)
χ_{sc}			0.74(4)

[a] Average value. [b] $\angle C(1)C(2)H$. [c] $\angle C(2)C(3)H$, not refined.

The molecular structures of each of the three compounds were refined by least-squares calculations on the intensity data with a non-diagonal weight matrix [27,28] and under the constraints of geometrically consistent r_a structures. For Me_2Zn five root mean square vibrational amplitudes were included in the refinement, for Et_2Zn ten amplitudes were refined, and for $n-Pr_2Zn$ eight. Those amplitudes that could not be refined, were fixed at the values calculated from the molecular force field. The resulting structure parameters and vibrational amplitudes are listed in Table 5 and Table 6, respectively.

Experimental radial distribution curves are compared to the theoretical curves calculated for the best models in Fig. 2. We consider the agreement satisfactory.

Table 6. Root mean square vibrational amplitudes, l, of Me_2Zn, Et_2Zn and $n-Pr_2Zn$, calculated from the molecular force fields (FF) and from least square refinements on the electron diffraction data (ED). All values in pm.

r_a	Me_2Zn $l(FF)$	$l(ED)$	Et_2Zn $l(FF)$	$l(ED)$	$n-Pr_2Zn$ $l(FF)$	$l(ED)$
$Zn-C$	5.6	5.0(2)	5.6	5.2(3)	5.8	4.7(8)
$C-C$	—	—	5.5	5.1(3)	5.6	4.2(7)
$C-H$	7.8	8.4(5)	7.9	7.5(4)	7.9	6.5(7)
$Zn\cdots C(2)$	—	—	8.5	10.0(4)	8.9	9.2(7)
$Zn\cdots C(3)_{sc}$	—	—	—	—	17.4	23.7(23)
$Zn\cdots C(3)_{ap}$	—	—	—	—	9.5	9.5[b]
$Zn\cdots H(1)$	12.5	12.2(5)	12.5	11.2(12)	13.2	13.3(46)
$C(1)\cdots C(3)$	—	—	—	—	7.3	7.3[b]
$C(1)\cdots C(1')$	7.6	7.8(9)	7.7	8.3(15)	8.0	7.1(21)
$C(1)\cdots C(2')$	—	—	12.8	17.4(17)	13.4	13.4[b]
$C\cdots H_{gem}$	15.4	17.9(23)[a]	10.9	9.6(10)	11.1	10.9(14)

[a] $C(1)\cdots H(1')$. [b] Not refined.

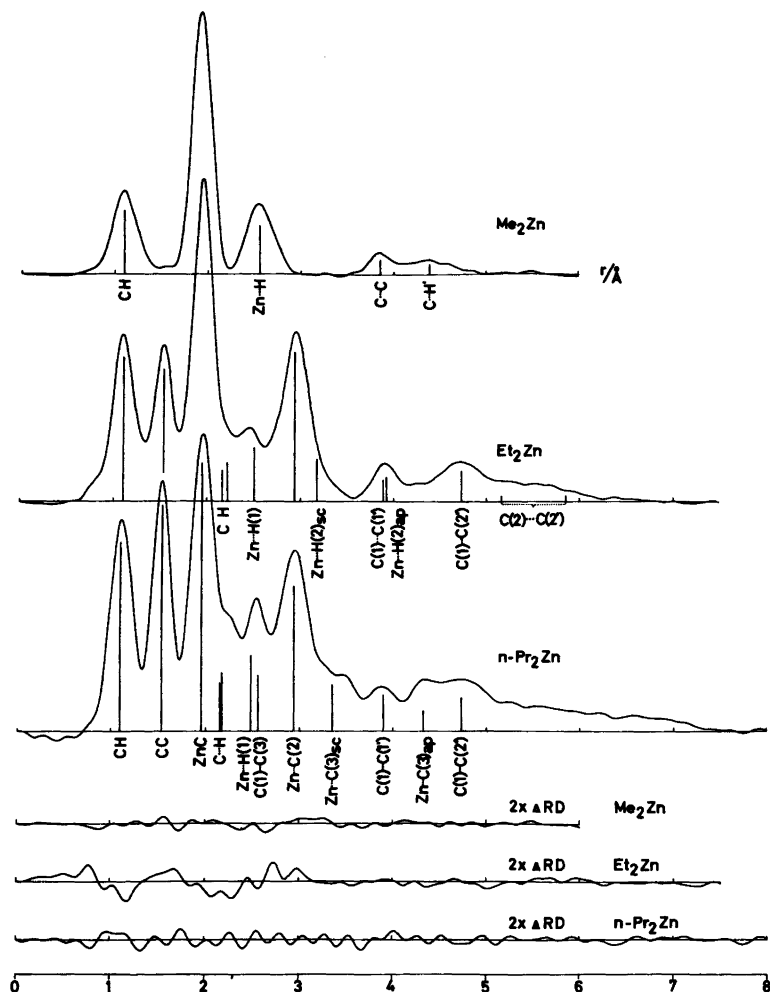*Fig. 2.* Experimental radial distribution (RD) curves for Me_2Zn, Et_2Zn, and n-Pr_2Zn. Artificial damping constant $k = 0.0025$ Å². Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Below: Difference between experimental RD curves and theoretical curves calculated for the best models.

RESULTS AND DISCUSSION

The bond distances and valence angles of Me_2Zn, Et_2Zn and n-Pr_2Zn are listed in Table 5. It is seen that the $Zn-C$ bond distance in Me_2Zn determined by gas phase electron diffraction is very close to the value obtained by rotational Raman spectroscopy, 192.9(4) pm.[5] It is significantly shorter than the $Zn-C$ bond distances in Et_2Zn and n-Pr_2Zn.

The valence angle $\angle ZnCC$ is about 114.5° in

both Et_2Zn and n-Pr_2Zn and seems reasonable considering the size of the Zn atom.

Somewhat surprisingly 74(4) % of the alkyl chains in n-Pr_2Zn are found in the *synclinal* conformation, corresponding to a free energy difference $\Delta\bar{G} = \bar{G}_{ap} - \bar{G}_{sc} = -RT\ln(\chi_{ap}/\chi_{sc}) = 2.9(6)$ kJ mol^{-1}. Introduction of the ratio of the partition functions, Q_{ap}/Q_{sc}, allows calculation of the energy difference at zero K:

$$\Delta \bar{E}^\circ = \bar{E}_{ap} - \bar{E}_{sc} = -RT \ln (\chi_{ap}/\chi_{sc}) + RT \ln (Q_{ap}/2Q_{sc}).$$

If the ratio is equal to unity, $\Delta \bar{E}^\circ = 1.0(6)$ kJ mol^{-1}. If the ratio is greater than unity, $\Delta \bar{E}^\circ$ increases. The ratio calculated from the approximate molecular force field in Table 4, $Q_{ap}/Q_{sc} = 1.25$, yields $\Delta \bar{E}^\circ = 1.5$ kJ mol^{-1}. The present study therefore suggests that the sc conformer is stabilized by a weak interaction between the Zn atom and the terminal methyl group, $Zn - C(3)_{sc} = 335$ pm.

The molecular force field of Me_2Zn in Table 3 is simpler than those obtained in previous normal coordinate analyses [9] and reproduces the observed frequencies [4] to the nearest cm^{-1}. The interaction terms $f'_{\alpha\alpha}$ and $f'_{\beta\beta}$ are necessary to reproduce the observed splitting of CH_3 deformation frequencies v_9/v_{13} and rocking frequencies v_{10}/v_{14}.

The equilibrium geometry obtained by ab $initio$ calculations on eclipsed Me_2Zn has $Zn - C = 197.7 \pm 3$ pm, $C - H = 108.5 \pm 2$ pm and $\angle ZnCH = 111.5 \pm 2°$, in reasonable agreement with the experimental results. Rigid rotation of the methyl groups into a staggered conformation changes the energy with less than 10^{-5} au (0.05 kJ mol^{-1}). Spectroscopic studies indicate that the barrier is negligible.[3]

The picture of the bonding emerging from the population analysis is similar to that obtained by others:[29-31] The $3d$ electrons are nonbonding, the orbital energies increasing in the order $\varepsilon_\delta < \varepsilon_\pi < \varepsilon_\sigma$ as expected from ligand field arguments and found by photoelectron spectroscopy.[30] The $Zn - C$ bonds are pure σ-bonds (the $p\pi - p\pi$ overlap population being negligible) polarized towards the C atoms. The gross atomic populations correspond to net atomic charges of $+0.92$ on Zn, -0.99 on C and $+0.18$ on H.

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