

On the Molecular Structure of Di-*t*-butyl Beryllium

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The electron scattering pattern from gaseous di-*t*-butyl beryllium has been recorded from 1.50 \AA^{-1} to 46.00 \AA^{-1} . It is consistent with a monomeric species with the CBeC valence angle equal to 180° . The other bond distances and valence angles are: Be-C = $1.699 \pm 0.003 \text{ \AA}$, C-C = $1.550 \pm 0.002 \text{ \AA}$, C-H = $1.126 \pm 0.002 \text{ \AA}$. $\angle \text{BeCC} = 110.4 \pm 0.1^\circ$, $\angle \text{CCH} = 110.5 \pm 0.5^\circ$. The *t*-butyl-groups appear to undergo virtually non-hindered rotation.

Molecular weight measurements show that di-*t*-butyl beryllium is monomeric in the vapour phase and in benzene solutions.¹ The Raman spectrum of the pure liquid and the IR absorption spectrum of the liquid and the gas are essentially consistent with a monomeric compound of symmetry D_{3d} .¹ This means that the CBeC valence angle is 180° and that the *t*-butyl groups either are staggered or undergo virtually non-hindered rotation.²

The molecular structure of the molecule in the staggered conformation is shown in Fig. 1. For the sake of clarity all hydrogen atoms except three have been omitted.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of *t*-butyl beryllium was a gift from professor Coates, Durham. The electron-diffraction pattern from the gas at about 30°C was recorded on the Oslo apparatus.³ Exposures were made with two nozzle to photographic

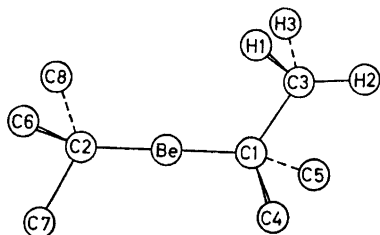


Fig. 1. The molecular structure of di-*t*-butyl beryllium in the staggered conformation.

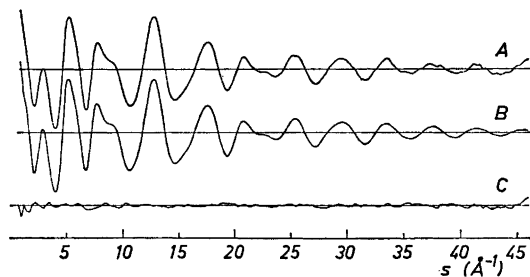


Fig. 2. Modified molecular intensity curves. A, experimental, B, theoretical calculated from the parameter values in Table 1, and C, difference curve.

plate distances, the two sets of plates thus obtained covered the diffraction ranges $s = 1 \text{ \AA}^{-1}$ to 20 \AA^{-1} and 7 \AA^{-1} to 48 \AA^{-1} . The diffraction parameter $s = (4 \pi \sin \theta)/\lambda$, where θ is half the diffraction angle and λ the electron wavelength. Four apparently faultless plates from each set were microphotometered and used for this study.

The experimental data were corrected and processed in the usual way.⁴ The resulting modified molecular intensity points from $s = 2.00 \text{ \AA}^{-1}$ to 46.00 \AA^{-1} are shown in Fig. 2 A.

Theoretical intensity curves were calculated from

$$I^{cc}(s) = \text{const} \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_c(s)||f_c(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

$$= \text{const} \sum_{i \neq j} g_{ij/cc}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2) \quad (1)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the inter-nuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \cdot \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j . It has been computed for H, Be, and C by the partial wave approximation method with a program written by Peacher.⁵

Theoretical RD curves were obtained by Fourier inversion of theoretical intensity curves. The molecular structure was refined by least-squares calculations on the intensity data.⁶

STRUCTURE ANALYSIS

A radial distribution (RD) curve obtained by Fourier inversion of the observed intensity is shown in Fig. 3 A. In this curve each interatomic distance R_{ij} in the molecule is represented by a peak centered at $r = R_{ij}$. The area under the peak is approximately proportional to $n_{ij}Z_iZ_j/R_{ij}$, where n_{ij} is the number of times the distance occurs and Z_i and Z_j the atomic numbers. The halfwidth of the peak is determined roughly by the root mean square amplitude of vibration, u_{ij} .

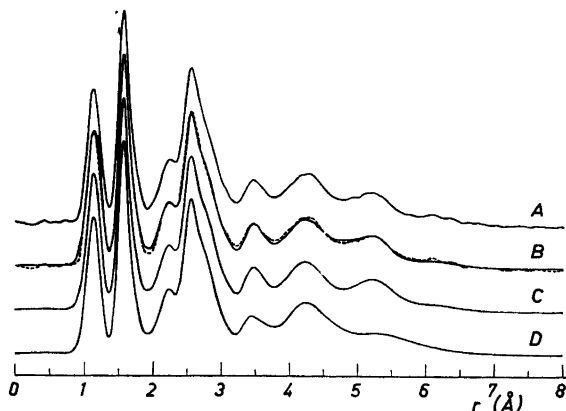


Fig. 3. Radial distribution (RD) curves. A, experimental, B, theoretical calculated from the parameter values given in Table 1 (with experimental curve stippled in), C, theoretical for eclipsed model, and D, theoretical for staggered model. $k = 0.001 \text{ \AA}^2$.

The experimental RD curve may be interpreted in the following way:

I. The peak at 1.13 \AA must correspond to the C—H bond distances.

II. The peak at 1.6 \AA is composite. The main contribution is from the six C—C bond distances expected near 1.55 \AA , but it also contains the two Be—C distances expected around 1.7 \AA .

III. The peak at 2.22 \AA corresponds to distances of the type C(1)···H(1).

IV. The peak extending from 2.4 to 3.0 \AA contains peaks representing distances of the three types C(3)···C(4), Be···C(3), and Be···H(1).

V. The peak at 3.5 \AA is due to distances of the type C(1)···C(2) and Be···H(2).

VI. The main contribution to the peak at 4.2 \AA is from distances of the type C(2)···C(3).

VII. The complex of peaks extending from 4.3 to 5.5 \AA is mainly due to distances of the type C(3)···C(6), C(3)···C(7), and C(3)···C(8).

The molecular structure was refined by least-squares calculations on the intensity data. It was assumed that the methyl groups are in the staggered position as shown in Fig. 1. It was further assumed that the *t*-butyl groups undergo non-hindered rotation, *i.e.* that the gas consists of an equimolar mixture of molecules in the eclipsed, staggered, and two intermediate conformations.

Unfortunately it was not possible to refine all *u*-values. The ones that could not be refined were assigned the values given in Table 1. The distances of type C(3)···C(6), C(3)···C(7), and C(3)···C(8) were assigned *u*-values ranging from 0.35 to 0.14 \AA .

The refinement converged to give the parameter values listed in Table 1. The standard deviations include the uncertainty in electron wavelength. The angles have not been corrected for shrinkage.

Fig. 2 B shows a theoretical modified molecular intensity curve and Fig. 3 B (full line) a theoretical RD curve calculated from the parameter values listed in Table 1. The agreement with experimental curves is very good.

Table 1. Interatomic distances, valence angles, and root mean square vibrational amplitudes of di-*t*-butyl beryllium. The standard deviations include the uncertainty in the electron wavelength. The distances are given as $r_g(1)$.¹² The angles have not been corrected for shrinkage. The values of dependent interatomic distances and assumed vibrational amplitudes are enclosed in parentheses.

	R (Å)	u (Å)
Be—C(1)	1.699 ± 0.003	0.048 ± 0.002
C(1)—C(3)	1.550 ± 0.002	0.054 ± 0.001
C(3)—H(1)	1.126 ± 0.002	0.079 ± 0.001
Be···C(3)	(2.671)	0.115 ± 0.006
Be···H(1)	(2.908)	(0.150)
Be···H(2)	(3.671)	(0.150)
C(1)···C(2)	(3.399)	(0.080)
C(3)···C(4)	(2.516)	0.074 ± 0.002
C(1)···C(6)	(4.200)	0.230 ± 0.014
C(1)···H(1)	(2.219)	0.110 ± 0.004
C(4)···H(1)	(2.785)	(0.15)
C(4)···H(2)	(2.765)	(0.15)
C(4)···H(3)	(3.512)	(0.10)
C(2)···H(1)	(4.215)	(0.22)
C(2)···H(2)	(5.274)	(0.22)
C(3)···C(6)	from (4.483)	from (0.35)
C(3)···C(7)		
C(3)···C(8)	to (5.342)	to (0.14)
∠BeCC	110.4 ± 0.1°	
∠CCH	110.5 ± 0.5°	

Fig. 3 C and D show theoretical RD curves computed for eclipsed and staggered molecular models. They differ from the non-hindered rotation model only in the region 3.5 to 6.5 Å. The RD curves for the three models in this region are shown on larger scale in Fig. 4. The eclipsed and non-hindered rotation models fit the experimental curve equally well, the staggered model is clearly unsatisfactory.

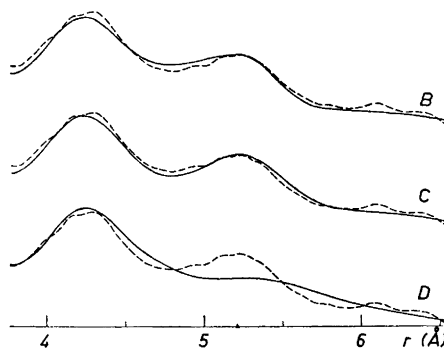


Fig. 4. Radial distribution (RD) curves in the region 4 to 7.5 Å. Stippled curves: Experimental. Full line: Theoretical, B, for non-hindered rotation, C, eclipsed model, and D staggered model. $k = 0.001$ Å².

DISCUSSION

The C—C bond distance and CCC valence angle found in di-*t*-butyl beryllium (1.550 ± 0.002 Å, $108.5^\circ \pm 0.1^\circ$) differ somewhat from the corresponding parameters in isobutane⁷ (1.525 ± 0.001 Å, $111.15^\circ \pm 0.10^\circ$) and *t*-butyl chloride⁸ (1.530 ± 0.002 Å, $110.9^\circ \pm 0.1^\circ$) by MW technique. The difference may be due to the different kind of averaging inherent in the two methods.¹²

The Be—C distance, 1.699 ± 0.003 Å is the first normal, single Be—C bond distance to be reported. It may be compared to the Be—C bond distance in crystalline Be(CH₃)₂, in which each beryllium atom is surrounded by four carbon atoms at the corners of a distorted tetrahedron, Be—C = 1.93 ± 0.02 Å.⁹ A difference of roughly the same magnitude is found between the Be—Cl distances in monomeric (1.75 ± 0.02 Å¹⁰) and polymeric (2.02 Å¹¹) BeCl₂. Our results in conjunction with the spectral studies of Coates, Roberts, and Downs¹ show that the *t*-butyl-groups undergo virtually non-hindered rotation, *i.e.* that the barrier to internal rotation is of the order of—or less than—the thermal energy available, 0.6 kcal/moles.

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REFERENCES

1. Coates, G. E., Roberts, P. D. and Downs, A. J. *J. Chem. Soc.* **1967** 1085.
2. Gutowsky, H. S. *J. Chem. Phys.* **17** (1949) 128.
3. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232.
4. Almenningen, A., Haaland, A. and Motzfeldt, T. *J. Organometal. Chem.* **7** (1967) 97.
5. Peacher, J. L. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4807.
6. Almenningen, A., Bastiansen, O., Seip, H. M. and Seip, R. *Acta Chem. Scand.* **18** (1964) 2115.
7. Lide, D. R. *J. Chem. Phys.* **33** (1960) 1519.
8. Lide, D. R. and Jeu, M. *J. Chem. Phys.* **38** (1963) 1504.
9. Snow, A. I. and Rundle, R. E. *Acta Cryst.* **4** (1951) 348.
10. Akishin, P. A. and Spiridonov, V. P. *Kristallografiya* **2** (1957) 475.
11. Rundle, R. E. and Lewis, P. H. *J. Chem. Phys.* **20** (1952) 132.
12. Bartell, L. S. *J. Chem. Phys.* **23** (1955) 1219.

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