

On the Molecular Structure of Dimanganese Decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$

A. ALMENNINGEN, G. G. JACOBSEN and
H. M. SEIP

Department of Chemistry, University of Oslo,
Blindern, Oslo 3, Norway

The crystal structure of $\text{Mn}_2(\text{CO})_{10}$ was published by Dahl *et al.*¹ in 1957. A more accurate structure based on three-dimensional data was later published by Dahl and Rundle.² $\text{Mn}_2(\text{CO})_{10}$ consists of discrete molecules of approximately D_{4d} symmetry (Fig. 1). The equatorial Mn—C

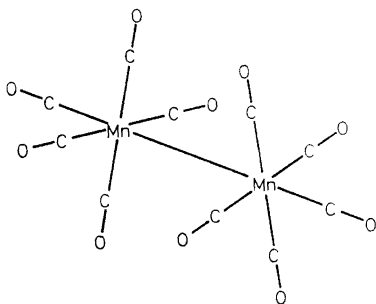


Fig. 1.

bonds were found to be bent inward towards the Mn—Mn bond. It is of interest to see if the bending is the same in the gaseous phase.

Brunvoll and Cyvin have calculated root-mean-square amplitudes of vibration (u) for $\text{Mn}_2(\text{CO})_{10}$ from spectroscopic data.³ Because of lack of spectral data their values must be regarded as rough approximations only. Recently additional data have been published,⁴ and the u value calculation will be improved. This investigation will then be continued, since better spectroscopic u values should make it possible to improve the present results considerably.

The sample of $\text{Mn}_2(\text{CO})_{10}$ was kindly sent us by Dr. T. H. Coffield, Ethyl Cooperation, Detroit. The electron diffraction photographs were taken with the Oslo apparatus.⁵ The modified molecular intensity calculated in the usual way,⁶ covered the s range 0.75 \AA^{-1} to

43.5 \AA^{-1} . The interval between the intensity points was 0.125 \AA^{-1} below $s=10.25 \text{ \AA}^{-1}$ and 0.25 \AA^{-1} above this value. The scattering amplitudes were calculated on a CDC 3300 computer with a program originally written by Peacher⁷ and later modified by T. Strand in this laboratory. Hartree-Fock potentials⁸ were used for C and O and a Hartree-Fock-Slater potential⁹ for Mn.

Preliminary results for the most important parameters are given in Table 1. These results were obtained by least-squares refinement on the intensity data neglecting the Bastiansen-Morino shrinkage effect.^{10,11} D_4 symmetry was assumed, and all the MnCO angles were fixed at 180° . By including the shrinkage effect estimated by calculating "average distances" (r_a) as described by Kuchitsu *et al.*,¹²⁻¹⁴ very similar results were obtained except that the torsional angle (φ) became 37.4° (2.6°). Only small changes in these parameters were obtained if $\angle \text{MnC}_{\text{eq}}\text{O}_{\text{eq}}$ was refined as an additional parameter. The O atoms were found to be bent slightly towards the Mn—Mn bond, so that the angle $\text{MnC}_{\text{eq}}\text{O}_{\text{eq}}$ was 178.6° (1.1°).

The results from the X-ray investigation² are also included in the table. The values obtained for $\angle \text{C}_{\text{ax}}\text{MnC}_{\text{eq}}$ are very nearly the same in the two investigations. There are some discrepancies in the bond distances. Our results for the Mn—C distances are in better agreement with the average Mn—C value of 1.858 \AA reported for $\text{HMn}(\text{CO})_5$ ¹⁵ (ED investigation) and the distances 1.805 \AA and 1.855 \AA obtained in $\text{Mn}(\text{CO})_5\text{Fe}(\text{CO})_4\text{Mn}(\text{CO})_5$ ¹⁶ (X-ray investigation). We find an Mn—Mn bond length which is significantly longer than the value found in the crystal according to the given standard deviations. Hamilton's R -factor test¹⁷ indicated that a model with an Mn—Mn distance of 2.923 \AA could be rejected at the 0.5 % level. A correction for the thermal motion would give a higher value for the Mn—Mn bond. Using the B values given in Ref. 2, we calculated the rigid body amplitudes.^{18,19} * The calculation indicated a correction of about 0.02 \AA for the Mn—Mn bond, but the agreement between calculated and observed amplitudes was not really satisfactory.

Even if the equilibrium conformation is staggered a φ value less than 45° will be

* The program has been modified by F. Gram at this University.

Table 1. Results of the present investigation compared to the results obtained by Dahl and Rundle.² The standard deviations given in parentheses have been multiplied by 10³.

	ED		X R
	r_a (Å)	u (Å)	(Å)
Mn—Mn	2.977 (11)	}	2.923 (3)
Mn—C _{ax}	1.803 (16)		1.792 (14)
Mn—C _{eq}	1.873 (5)		1.830 (8)
C—O	1.147 ₀ (2)		1.156 (7)
	degrees		degrees
$\angle C_{ax}MnC_{eq}$	93.4 (0.5)		93.8 (0.4)
φ	42.4 (7.4)		≈ 45

observed by electron diffraction because of the oscillations around the Mn—Mn bond. The value obtained for φ shows that the rotation is not free. We tried to determine the barrier by the method described by Almenningen *et al.*²⁰ However, it turned out that fairly good spectroscopic amplitudes were necessary to obtain a reasonably accurate barrier.

The C_{ax}MnC_{eq} angles are significantly greater than 90° also in the gaseous phase. The C_{ax}—Mn distance is shorter than C_{eq}—Mn. There seems to be a significant difference between our result for the Mn—Mn bond length and the value obtained in the crystal, but this distance is difficult to determine by electron diffraction because of the great overlap with other distances. There is no evidence for deviation from D_{4d} symmetry, and the barrier to internal rotation seems to be about 2 kcal/mole or more.

- Dahl, L. F., Ishishi, E. and Rundle, R. E. *J. Chem. Phys.* **26** (1957) 1750.
- Dahl, L. F. and Rundle, R. E. *Acta Cryst.* **16** (1963) 419.
- Brunvoll, J. and Cyvin, S. J. *Acta Chem. Scand.* **22** (1968) 2709.
- Adams, D. M. and Squire, A. *J. Chem. Soc. A* **1968** 2817.
- Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand.* **9** (1955) 232.
- Seip, H. M. In *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967.

- Peacher, J. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4809.
- Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
- Cox, H. L. and Bonham, R. A. *J. Chem. Phys.* **47** (1967) 2599.
- Almenningen, A., Bastiansen, O. and Munthe-Kaas, M. *Acta Chem. Scand.* **10** (1956) 261.
- Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo 1968.
- Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* **36** (1962) 1108.
- Kuchitsu, K. and Konaka, S. *J. Chem. Phys.* **45** (1966) 4342.
- Kuchitsu, K., Fukuyama, T. and Morino, Y. *J. Mol. Struct.* **1** (1967—68) 463.
- Robiette, A. G., Sheldrick, G. M. and Simpson, R. N. F. *Chem. Commun.* **1968** 506.
- Agron, P. A., Ellison, R. D. and Levy, H. A. *Acta Cryst.* **23** (1967) 1079.
- Hamilton, W. C. *Acta Cryst.* **18** (1965) 502.
- Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 754.
- Hirshfeld, F. L., Sandler, S. and Schmidt, G. M. J. *J. Chem. Soc.* **1963** 2108.
- Almenningen, A., Hartmann, O. Å. and Seip, H. M. *Acta Chem. Scand.* **22** (1968) 1013.

Received January 18, 1969.