The Crystal Structure of Azulene Dimolybdenum Hexacarbonyl†

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AZULENE DIMOLYBDENUM HEXACARBONYL (I), $C_{10}H_8Mo_2(CO)_6$, was first prepared by Burton, Pratt, and Wilkinson,[1] and subsequently investigated by King and Bisnette,[2] with various structures being proposed for the complex.[1–3] More recently, Churchill[4] has determined the structure of an iron carbonyl complex of azulene, $C_{10}H_8Fe_2(CO)_5$, shown to be (II). We have investigated the crystal structure of (I) to determine the molecular geometry.

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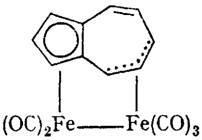
† When this study was essentially complete, we heard that Professor Melvyn R. Churchill, Harvard University, Cambridge, Massachusetts, was completing a study on a different crystalline modification of azulene dimolybdenum hexacarbonyl. The results of Professor Churchill's work on azulene dimolybdenum hexacarbonyl and on guaiazulene dimolybdenum hexacarbonyl, which does not exhibit random disorder, are presented in the preceding Communication. We thank Professor Churchill for sending his results to us prior to publication.

The compound was prepared by the method of Burton and his co-workers,[1] but initially only extremely fine needles were obtained. These were disslved in methylene dichloride and upon evaporation, some larger needles were found among the finer material. The crystal which we have studied[†] belongs to the monoclinic system, with $a = 9{\cdot}30$, $b = 12{\cdot}81$, $c = 14{\cdot}13$ Å, and $\beta = 111°20'$, as determined from precession photographs with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). There are four molecules of $C_{10}H_8Mo_2(CO)_6$ in the unit cell and the space group is $P2_1/c$. Intensity data were collected by equi-inclination Weissenberg photographs (Mo-K_α radiation) and visual estimations. The data fade out quite rapidly and only 875 independent, non-zero reflexions were obtained. After location of the molybdenum atoms and the atoms of the carbonyl groups, it became obvious that the hydrocarbon crystallized in a statistically disordered fashion, reminiscent of azulene itself.[5] Inclusion of the atoms of the azulene skeleton in a 2-fold disordered orientation, with C-1, C-2, C-3, C-5, C-6, and C-7 overlapping C-5′, C-6′, C-7′, C-1′, C-2′, and C-3′ respectively, followed by a full-matrix least-square analysis has given, at the present stage of refinement, an R-factor of 0·085 on all observed reflexions. A drawing of the molecular structure viewed along the c-axis is shown in the Figure.



(II)

The packing disorder and the limited data available to us restrict the conclusions which can be drawn concerning the bonding. The chemical structure consists of two $Mo(CO)_3$ groups on the *same* side of the azulene molecule with a Mo–Mo distance of 3·24 Å, agreeing well with similar distances found in other structures.[6] The structure of the complex in the crystal can be considered to have an approximate 2-fold rotation axis, bisecting the Mo–Mo bond and relating an azulene molecule in one orientation to one in the other orientation.

While the standard deviations of the Mo–C (0·03—0·04 Å) and C–C (0·06—0·08 Å) bond distances are very high, a few general conclusions can be drawn about the bonding. One molybdenum atom apparently complexes to a five-membered ring giving equal Mo–C distances of 2·34 Å (average of ten such distances ranging from 2·22—2·44 Å). The other molybdenum atom complexes to the seven-membered ring, giving approximately equal Mo–C distances to the five atoms which are not part of the five-membered ring, but further structural details must be inferred from the results of the study on guaiazulene dimolybdenum hexacarbonyl,[†] where no random disorder occurs. The angle between the best plane through the atoms of the five-membered ring and that through the five complexing atoms of the seven-membered ring is 15°. The conclusions drawn from this study are in general agreement with the results of the study on the triclinic modification where a similar structural disorder is found, and with the structure of guaiazulene dimolybdenum hexacarbonyl.[†]

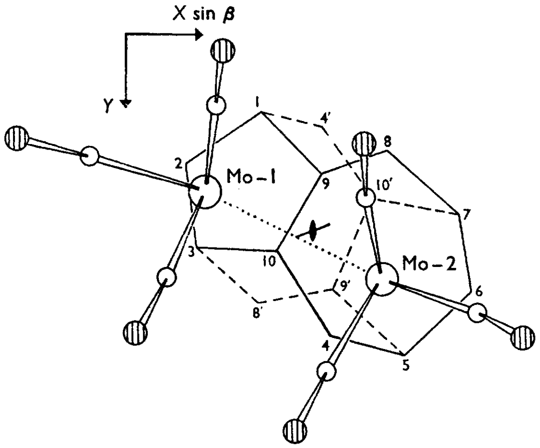


FIGURE. *A view of the structure along the* c-*axis. One orientation of the azulene molecule is shown as a solid line, the other by a discontinuous line. The pseudo* 2-*fold axis relating the two orientations, and bisecting the* Mo-1–Mo-2 *bond is shown.*

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[1] R. Burton and G. Wilkinson, *Chem. and Ind.*, 1958, 1205; R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 4290.

[2] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 475.

[3] M. A. Bennett in "Advances in Organometallic Chemistry," Academic Press, New York, 1966, Vol. 4, p. 353.

[4] M. R. Churchill, *Chem. Comm.*, 1966, 450; *Inorg. Chem.*, 1967, **6**, 190.

[5] J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Cryst.*, 1962, **15**, 1.

[6] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809; R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 1965, **87**, 2576.