

The Crystal Structure of Azulene Dimolybdenum Hexacarbonyl*

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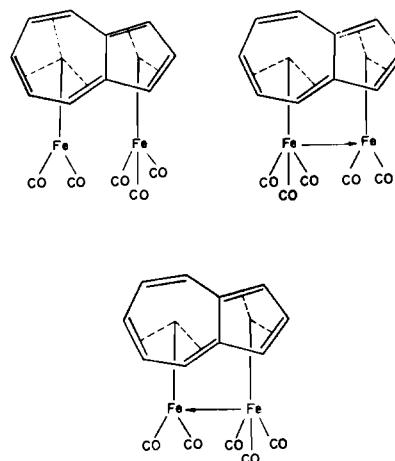
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The single crystal x-ray structure determination of azulene dimolybdenum hexacarbonyl has been completed. The compound was found to crystallize in the triclinic space group $P\bar{1}$ with $a=9.791$, $b=12.402$, $c=6.995$ Å, $\alpha=87.68$, $\beta=113.11$, $\gamma=86.75^\circ$ with two molecules per unit cell giving a calculated density of 2.09 g/cc. Least squares refinement using the 3545 observed reflections collected by counter methods gave a final conventional R-factor of 5.8%. $C_{10}H_8Mo_2(CO)_6$ exists as molecular units. One molybdenum is π -bonded to the five-membered azulene ring and to three carbonyls. The other molybdenum is bonded strongly to the end three carbons of the seven-membered ring (2.336 Å) and more weakly to the next two (2.499 Å) as well as to the three carbonyls. The two molybdenum atoms are bonded to one another by a long metal-metal of 3.226 Å. The azulene ring is disordered as it is in solid molecular azulene. The azulene ring is not planar, the dihedral angle between the seven and five-membered rings being about 15° , the rings being bent away from the metals. The non-planarity of the ring and semi-allylic character of the molybdenum bond to the seven-membered ring are apparently compromises necessitated by the molybdenum-molybdenum bond.

Introduction

In 1958, the preparation of several π -bonded dimetallic azulene complexes were reported by Burton and Wilkinson.^{1,2} The diiron pentacarbonyl complex, in particular, was studied in great detail³ and several possible structures were proposed (see Figure 1). A recent determination of the iron complex⁴ has shown the second structure to be approximately correct. It was found that the five-membered azulene ring functions as a π -cyclopentadienyl ligand and that an iron atom is bonded to an allylic three carbon region of the seven-membered ring.

King and Bisnette⁵ have conjectured that the related azulene dimolybdenum hexacarbonyl contains a Mo- π -cyclopentadienyl bond and a molybdenum

Figure 1. Proposed structures of $C_{10}H_8Fe_2(CO)_6$.

bonded over a five carbon region of the seven-membered ring. Because of its limited solubility in all solvents, little spectral evidence could be presented for this structure. Therefore we decided to undertake a single crystal x-ray study of this molybdenum complex.

As we were preparing this paper for publication, a note appeared on this complex by Churchill and Bird.⁶ Their preliminary results appear to agree quite well with ours.

Experimental Section

A sample of the compound was kindly supplied by R. B. King, and dark red crystals were obtained by recrystallization from a chloroform solution. Microscopic examination revealed that the crystals were prismatic in shape with sharply defined faces. A crystal was selected and mounted in a capillary, and Weissenberg and precession pictures were taken. All photographs showed an absence of mirroring implying a triclinic space group. The space group was assumed to be $P\bar{1}$ from an analysis of the Patterson maps and later confirmed by successful refinement in this space group. There are two molecules per unit cell giving a reasonable density of 2.09 g/cc consistent with observed densities of

(*) Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission.

(1) R. Burton and G. Wilkinson, *Chem. Ind.* (London), 1205 (1958).

(2) R. Burton, M. L. N. Green, E. W. Abel, and G. Wilkinson, *ibid.*, 1592 (1958).

(3) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(4) M. R. Churchill, *Inorg. Chem.*, 6, 190 (1967).

(5) R. B. King and M. B. Bisnett, *Inorg. Chem.*, 4, 475 (1965).

(6) M. R. Churchill and P. H. Bird, *Chem. Comm.*, 746 (1967).

related compounds. The conventional reduced cell⁷ lattice parameters are

$$\begin{array}{ll} a = 9.791 \pm 0.001 \text{ \AA} & \alpha = 87.68 \pm 0.01^\circ \\ b = 12.402 \pm 0.001 & \beta = 113.11 \pm 0.01 \\ c = 6.995 \pm 0.001 & \gamma = 86.75 \pm 0.01 \end{array}$$

The lattice constants were determined by a least squares refinement⁸ of 16 reflections observed on the single crystal orienter using CrK α radiation. The orienter was previously aligned with an aluminum single crystal.

Complete three-dimensional data to $\sin \frac{\theta}{\lambda} = 0.704$

were taken with zirconium-filtered, molybdenum K α radiation using a General Electric XRD-5 x-ray unit equipped with a single crystal orienter. Using a 40-sec stationary crystal-stationary counter counting technique, intensities for 4932 reflections were obtained. A number of backgrounds were compiled for different values of chi and phi and were plotted as a function of two-theta. A slight phi dependence was observed and three background curves were made up. Background, streak, absorption, polarization and Lorentz corrections were made on the intensities. The streak corrections were made using a modification of the method of Williams.⁹ A correction was also made to convert the peak height intensities to integrated intensities using the expression given by Alexander and Smith.¹⁰

Structural Refinement

A Patterson map was generated using all the collected intensities. The resulting map contained five large peaks considered to be molybdenum-molybdenum vectors. These peaks occurred on or near the $W=0$ section and could only be interpreted as resulting from a set of approximately C-centered molybdenum atoms in a cell containing a center of symmetry. A check of the intense reflections revealed that all but a very few corresponded to the $h+k=2n$ type. The molybdenum positional parameters were thus determined and two cycles of positional refinement on the molybdenum atoms, using the 1500 most intense reflections, produced a conventional R-factor ($R = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}$) of 0.34. It was thought that difficulties might be encountered in finding the carbonyls and rings because of the presence of a false image arising from the pseudo C-centering. However, the least squares refinement of the molybdenum positions succeeded in destroying the pseudo-symmetry. Faint C-centered images of carbonyls could be seen in an electron density map calculated

from the refined molybdenum positions but no difficulty was encountered in finding one set of carbonyls and the azulene ring in the map. Two cycles of positional refinement on all atoms reduced the R-factor to 0.181. Further isotropic refinement on all atoms gave an agreement of 0.0986 for the 1500 most intense reflections. An electron density map generated from these parameters showed several extra peaks occurring near the azulene ring. These peaks could be readily interpreted as resulting from disorder in the azulene ring. Judging from the heights of the disordered atoms, it appeared as if the disorder was 50-50. The disorder was only visible in the four central carbons; as can be seen in Figure 2, the end three carbons of the azulene rings apparently coincided in the disordered images. In fact, attempts were made to insert half carbons for other carbon atoms in the azulene ring and further resolve the disorder.

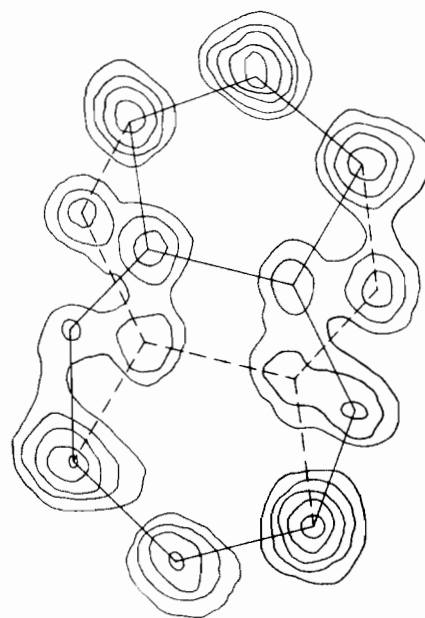


Figure 2. Azulene ring disorder in $C_{10}H_8Mo_2(Co)_6$.

However, in all these cases the reliability factor diverged with additional refinement attempts. Refinement on the disordered model, with molybdenums anisotropic, reduced agreement factor to 0.0421 for the 1500 most intense reflections. At this point approximately 50 reflections were removed for which the agreement between F_0 and F_c was poor. Since the structure was over-determined and since the data were taken by stationary methods, where errors in settings are less likely to be caught, it was felt that this procedure was justified. Fritchie¹¹ further justifies this action by pointing out that a few bad reflections can several affect bond distances and thus, if at all questionable, should be rejected. Refinement continued for two cycles, with the molybdenum atoms anisotropic, using the remaining 3545 observed reflections, and a final agreement factor of

(7) S. L. Lawton and R. A. Jacobson, «The Reduced Cell and its Crystallographic Applications», USAEC Rept. IS-1141 (1965).

(8) D. E. Williams, «LCR-2, A Fortran Lattice Constant Refinement Program», USAEC Rept. IS-1052 (1964).

(9) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1660 (1964).

(10) L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962).

(11) C. Fritchie, *Trans. of the Am. Cryst. Ass.*, **1**, 30 (1965).

Table I. Final Parameters and Standard Deviations from Least Squares Refinement of $C_{10}H_8Mo_2(CO)_6$.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B ^a	$\sigma(B)$
Mo1	0.07975	0.00006	0.21386	0.00004	-0.04246	0.00008	—	—
Mo2	0.40684	0.00006	0.28941	0.00004	-0.00520	0.00007	—	—
C1	-0.04728	0.00086	0.28845	0.00062	-0.36471	0.00114	4.628	0.292
C2	-0.07348	0.00089	0.17759	0.00063	-0.36489	0.00118	4.841	0.306
C3	0.04690	0.00084	0.09858	0.00059	-0.32328	0.00110	4.191	0.275
C10	0.17470	0.00146	0.16871	0.00106	-0.29576	0.00189	3.440	0.446
C4	0.32723	0.00156	0.12847	0.00114	-0.22973	0.00205	3.836	0.486
C5	0.43937	0.00081	0.17886	0.00059	-0.27264	0.00108	4.242	0.272
C6	0.46031	0.00082	0.28813	0.00058	-0.30411	0.00109	4.288	0.275
C7	0.34213	0.00079	0.36734	0.00055	-0.32662	0.00105	3.987	0.257
C8	0.20550	0.00143	0.37362	0.00108	-0.29841	0.00187	3.435	0.440
C9	0.11618	0.00147	0.28573	0.00109	-0.32126	0.00185	3.295	0.431
C10'	0.20155	0.00134	0.09878	0.00100	-0.25461	0.00176	2.942	0.399
C4'	0.28088	0.00142	0.18448	0.00103	-0.28429	0.00183	3.056	0.436
C8'	0.22078	0.00136	0.30034	0.00101	-0.31570	0.00175	3.016	0.400
C9'	0.07646	0.00170	0.34144	0.00126	-0.31190	0.00216	4.069	0.536
C11	0.06555	0.00070	0.34154	0.00051	0.13191	0.00094	3.412	0.221
O1	0.04846	0.00059	0.41706	0.00042	0.22810	0.00077	4.858	0.207
C12	-0.08578	0.00077	0.17178	0.00055	0.03597	0.00102	3.906	0.251
O2	-0.17795	0.00067	0.14280	0.00045	0.08647	0.00087	5.909	0.244
C13	0.19370	0.00070	0.11189	0.00050	0.17540	0.00093	3.284	0.217
O3	0.25150	0.00057	0.04685	0.00041	0.29236	0.00076	4.791	0.205
C14	0.49196	0.00071	0.18462	0.00050	0.21757	0.00094	3.319	0.220
O4	0.55065	0.00058	0.12248	0.00041	0.34244	0.00077	4.859	0.205
C15	0.60141	0.00079	0.34303	0.00055	0.11345	0.00101	3.939	0.246
O5	0.71913	0.00065	0.37416	0.00045	0.18922	0.00084	5.469	0.226
C16	0.35863	0.00070	0.41144	0.00052	0.15977	0.00094	3.322	0.218
O6	0.33737	0.00058	0.48768	0.00043	0.24875	0.00078	4.903	0.208

^a Anisotropic thermal parameters: β_{11} , β_{22} , β_{33} , β_{12} , β_{13} , β_{23} . Mo1: 0.01047(8), 0.00500(4), 0.01584(12), -0.00093(4), 0.00486(7), -0.00089(5); Mo2: 0.00924(7), 0.00562(4), 0.01703(13), -0.00107(4), 0.00182(7), -0.00080(5).

0.061 was obtained. Before the last cycle, a weighting scheme check was run and the weights were found to be inadequate. They were changed such that a plot of $\Delta^2\omega$ (where $\Delta^2 = (|F_o| - |F_c|)^2$ and ω is the weighting factor) versus average F_o for groups of 100 reflections gave a straight, horizontal line. The final weighted R-factor with these weights was 0.058. The final parameters can be seen in Table I and the molecular structure is shown in Figure 3. The final distances and angles with standard deviations were calculated using Busing's ORFFE program¹² and are listed in Table II. In Table III are listed the observed and calculated structure factors. A final electron density map clearly showed anisotropic motion in the carbonyl oxygens, but no evidence could be seen for disorder in any but the previously mentioned four atoms. No evidence of the azulene

hydrogens could be seen, possibly because of the disorder. Because of the great length of time required per least squares cycle, anisotropic refinement of the light atoms was not attempted.

Results and Discussion

The structure of azulene dimolybdenum hexacarbonyl can be profitably compared with π -cyclopentadienyl molybdenum tricarbonyl dimer.¹³ The dimer is held together solely by a long molybdenum-molybdenum bond of 3.222 Å, which compares very well with the 3.262 Å distance observed in the azulene compound. The other distances compare very favorably also: 2.345 Å molybdenum-ring carbon and 1.960 Å molybdenum-carbonyl average distances compared to 2.325 and 1.968 Å, respectively, observed in the azulene complex. Thus, the moiety associated with the molybdenum bound to the five-membered ring of azulene can be considered as virtually identical with half of the dimer.

The other molybdenum-carbon bonds fall into three classes averaging 2.336, 2.499, and 2.940 Å. The bond order of the second relative to the first, using Pauling's formula is 1/2, while the third to the first is very small. Thus in this case, the molybdenum can be considered to bond to the π -system of the end three carbons in a similar fashion to that which occurs in π -cycloheptatrienyl- π -cyclopentadienyl

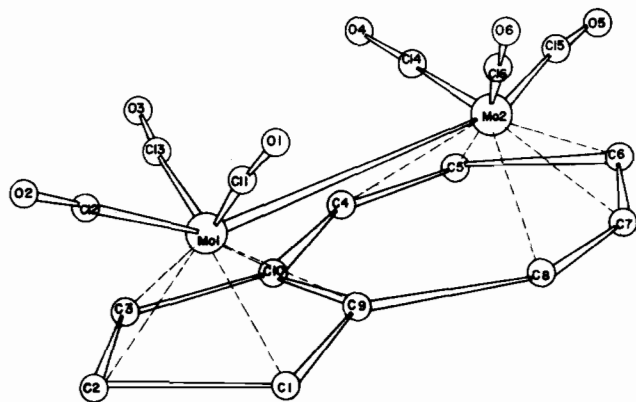


Figure 3. The molecular structure of $C_{10}H_8Mo_2(CO)_6$.

(12) W. R. Busing and H. A. Levy, USAEC Rept. ORNL 59-12-3 (1959).

(13) F. C. Wilson and D. R. Shoemaker, *J. Chem. Phys.*, 27, 809 (1957).

Table II. Distances and Angles in $C_{10}H_8Mo_2(CO)_6$ and their Standard Deviations

Atom 1	Atom 2	Distance	Error	Atoms			Angle	Error
Mo1	Mo2	3.2602 Å	0.0009 Å	Mo1	Mo2	C14	87.44°	0.22'
Mo1	C11	1.982	0.008	Mo1	Mo2	C15	159.80	0.24
Mo1	C12	1.951	0.008	Mo1	Mo2	C16	85.12	0.22
Mo1	C13	1.981	0.007	Mo2	Mo1	C11	85.63	0.22
Mo2	C14	1.980	0.007	Mo2	Mo1	C12	160.28	0.22
Mo2	C15	1.932	0.009	Mo2	Mo1	C13	84.33	0.22
Mo2	C16	1.980	0.008	C11	Mo1	C12	82.65	0.32
Mo1	C1	2.361	0.009	C11	Mo1	C13	97.76	0.30
Mo1	C2	2.298	0.009	C12	Mo1	C13	81.63	0.31
Mo1	C3	2.334	0.009	C14	Mo2	C15	81.03	0.32
Mo1	C10	2.273	0.015	C14	Mo2	C16	97.17	0.30
Mo1	C9	2.316	0.015	C15	Mo2	C16	79.96	0.32
Mo2	C4'	2.228	0.014	Mo1	C11	O1	176.05	0.67
Mo2	C5	2.362	0.009	Mo1	C12	O2	176.54	0.74
Mo2	C6	2.309	0.008	Mo1	C13	O3	174.28	0.68
Mo2	C7	2.350	0.008	Mo2	C14	O4	174.88	0.67
Mo2	C8'	2.307	0.014	Mo2	C15	O5	178.40	0.73
Mo1	C10'	2.503	0.014	Mo2	C16	O6	174.13	0.67
Mo1	C9'	2.500	0.017	C1	C2	C3	119.60	0.87
Mo2	C4	2.500	0.016	C2	C3	C10	100.68	0.88
Mo2	C8	2.491	0.015	C3	C10	C9	109.53	1.17
Mo1	C4'	2.941	0.015	C10	C9	C1	106.75	—
Mo1	C8'	2.955	0.014	C9	C1	C2	103.42	0.95
Mo2	C10	2.939	0.015	C10	C4	C5	123.49	1.45
Mo2	C4	2.923	0.015	C4	C5	C6	133.88	1.02
C11	O1	1.162	0.009	C5	C6	C7	119.10	—
C12	O2	1.140	0.010	C6	C7	C8	136.28	0.98
C13	O3	1.141	0.008	C7	C8	C9	124.74	1.40
C14	O4	1.152	0.009	C8	C9	C10	124.71	1.42
C15	O5	1.165	0.010	C9	C10	C4	126.34	—
C16	O6	1.151	0.009	C6	C7	C8'	101.46	—
C1	C2	1.419	0.012	C7	C8'	C4'	108.96	—
C5	C6	1.423	0.012	C8'	C4'	C5	107.60	—
C2	C3	1.403	0.012	C4'	C5	C6	102.81	—
C6	C7	1.401	0.011	C2	C3	C10'	135.76	0.98
C3	C10	1.516	0.017	C3	C10'	C4'	124.50	1.28
C7	C8'	1.506	0.016	C10'	C4'	C8'	125.05	1.34
C10	C4	1.424	0.022	C4'	C8'	C9'	124.81	1.41
C8'	C9'	1.434	0.018	C8'	C9'	C1	127.12	—
C4	C5	1.404	0.018	C9'	C1	C2	133.40	—
C9'	C1	1.338	0.019					
C10	C9	1.504	0.021					
C4'	C8'	1.496	0.020					
C3	C10'	1.393	0.016	Plane 1	Plane 2	Dihedral angle	Error	
C7	C8	1.277	0.017					
C10'	C4'	1.417	0.020	C1-C2-C3	C5-C6-C7	166.27°	1.22	
C8	C9	1.414	0.022	C1-C3-C9	C5-C6-C7	167.87	1.03	
C4'	C5	1.483	0.017	C1-C2-C3	C4-C6-C8	161.07	0.98	
C9	C1	1.485	0.018	C5-C6-C7	C2-C10'-C9'	162.26	0.91	

molybdenum dicarbonyl.¹⁴ Yet the bonding cannot be considered to only involve an allylic π -bond because some bonding to the π -system of all five end carbon atoms must be considered.

This rather unique bonding by the molybdenum to the seven-membered ring can be seen to arise as a result of the 3.262 Å molybdenum-molybdenum bond. Because one molybdenum atom bonds equivalently to the five-membered ring, the other molybdenum is forced to assume a π -bonding position close to end of the seven-membered ring. The azulene appears to be attempting to compensate for this by bending in the middle such that the ends of the rings move away from the metals (Tables II and IV). This molybdenum atom can thus bond more effectively over a broader portion of the seven-membered ring. Interestingly, the end of the azulene ring was found to

bend toward the metal atoms in azulene diiron pentacarbonyl. In this case the much shorter metal-metal bond (2.782 Å) caused this distortion to be favorable.

The disorder in the azulene ring is similar to that found in molecular azulene.¹⁵ The distances and angles reported for azulene complexed with *s*-trinitrobenzene by Hanson¹⁶ can be compared to those found in this determination. In the former complex, the azulene ring was disordered to the extent of only 7%. In his determination, the C(9)-C(10) distance was found to be 1.498 Å, while the other carbon-carbon distances were all within 0.008 Å of the 1.395 average. Comparing his results with this determination, it appears as if the distances and angles found for the azulene moiety here are compromises due

(14) R. B. Kind and M. B. Bisnett, *Tetrahedron Letters*, 18, 1137 (1963).

(15) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and P. G. Watson, *Acta Cryst.*, 15, 1 (1962).

(16) A. W. Hanson, *Acta Cryst.*, 19, 19 (1965).

Table IV. Least Squares Planes in $C_{10}H_8Mo_2(CO)_6$

Plane No.	Generated from						
1	rings 1 and 2*	$-0.162 X + 0.039 Y + 0.986 Z + 2.021 = 0.0$					
2	ring 1	$-0.187 X + 0.052 Y + 0.981 Z + 2.009 = 0.0$					
3	ring 2	$-0.125 X + 0.017 Y + 0.992 Z + 2.146 = 0.0$					
4	7-member ring 2	$-0.143 X - 0.041 Y + 0.989 Z + 2.297 = 0.0$					
5	5-member ring 2	$-0.132 X + 0.108 Y + 0.985 Z + 1.685 = 0.0$					
6	5-member ring 1	$-0.258 X - 0.039 Y + 0.965 Z - 2.225 = 0.0$					

Name	Distance from plane in Å					
	(1)	(2)	(3)	(4)	(5)	(6)
C1	-0.0915	-0.0313	-0.0763	-0.0573	-0.2671	0.0426
C2	-0.1986	-0.1639	-0.1421	-0.0523	-0.4552	0.0076
C3	-0.1307	-0.1289	-0.0265	0.0364	-0.3471	-0.0568
C10	0.1798	0.1662	0.3032	0.2816	0.0699	0.0533
C10'	0.0083	0.0147	0.1014	0.0584	-0.0785	-0.1095
C4	0.2582	0.2391	0.3863	0.2798	0.2543	-0.0443
C4'	-0.0063	-0.0073	0.0950	-0.0152	-0.0082	-0.2706
C5	-0.0962	-0.1157	0.0292	-0.1671	0.0134	-0.5703
C6	-0.2028	-0.1971	-0.1176	-0.3820	-0.0138	-0.7448
C7	-0.1412	-0.1026	-0.1041	-0.3425	0.0075	-0.5521
C8	0.2026	0.2583	0.2169	0.0534	0.2527	-0.0241
C8'	-0.0206	0.0144	0.0259	-0.1099	0.0012	-0.2448
C9	0.0334	0.0759	0.0713	0.0013	-0.0284	-0.0467
C9'	0.2056	0.2670	0.2150	0.1398	0.1449	0.1617
Mo1	1.9013	1.9350	1.9523	1.9494	1.7472	1.9236
Mo2	1.9074	1.9255	1.9729	1.7492	2.0305	1.4691
C11	3.2362	3.2944	3.2387	2.9870	3.3770	2.8406
O1	3.9615	4.0434	3.9266	5.6517	4.1213	3.5784
C12	2.5838	2.5966	2.6507	2.2949	2.8678	1.8787
O2	3.0194	3.0290	3.0875	2.6525	3.3995	2.1543
C13	3.2233	3.2095	3.3549	3.1244	3.3295	2.7287
O3	3.9476	3.9140	4.0878	3.8799	4.0507	3.4074
C14	3.1585	3.1579	3.2587	3.2510	3.0108	3.0840
O4	3.8228	3.8015	3.9533	3.9502	3.6700	3.7046
C15	2.5614	2.6041	2.6069	2.7175	2.2558	2.8285
O5	2.9706	3.0171	3.0086	3.1914	2.5771	3.3766
C16	3.2666	3.3383	3.2569	3.2044	3.1572	3.2846
O6	4.0351	4.1301	3.9884	3.9110	3.9467	4.0616

* Ring 1: image 1; ring 2: image 2 (see Figure 4).

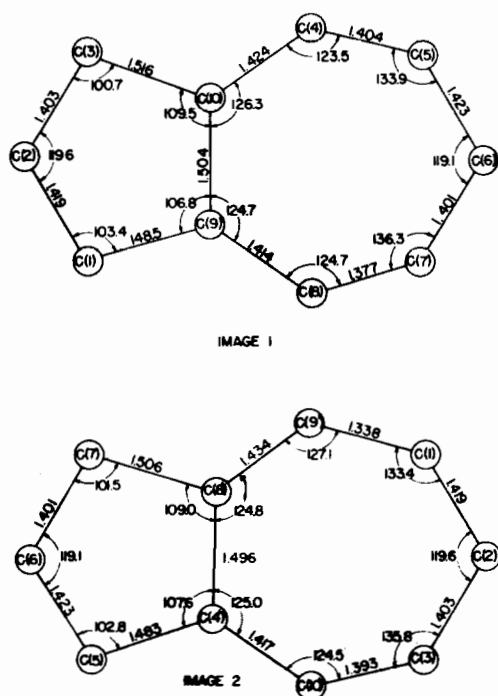


Figure 4. Distances and angles in the disordered azulene rings.

to the fact that the electron density distribution results from the partial superposition of two images. That is, in the azulene-molybdenum molecule, the C(1)–C(2)–C(3) and C(5)–C(6)–C(7) angles were found to be 119.6 and 119.1°, respectively, which represents an average of the 110.16 and 129.47° for the corresponding angles found by Hanson. Thus it must be concluded that the two azulene images in this structure, while in excellent agreement (Figure 4), represent only a good compromise to the actual ring distances and angles.

The disorder in this complex can be attributed to the symmetric positions of the molybdenums with respect to the ring. In the iron-azulene complex one iron atom is off the azulene mirror plane and disorder is then less likely.

The molybdenum-carbonyl bonding is in good agreement with such bonding observed in other compounds.¹³⁻¹⁸ Upon examination of Table II, it is seen that the two carbonyl opposite the metal-metal bond have significantly shorter metal-carbon distances. Such shortening has been observed in other compounds, such as in π -cyclopentadienyl molybdenum tricarbonyl dimer, and we feel it is real.

(17) J. A. Ibers and W. C. Hamilton, *J. Chem. Phys.*, **44**, 1748 (1966).
 (18) J. D. Dunitz and P. Pauling, *Helv. Chem. Acta*, **43**, 2188 (1960).