A constrained refinement was carried out, giving $C-C=1.4056\pm0.0015$ Å and $C-D=1.073\pm0.003$ Å, but the R values obtained by the rigid-body thermal parameters and then by variable thermal parameters were 6.0 and 5.8% respectively. These are both significantly poorer than previous R values on the 2% level of the F distribution. We therefore conclude that the extra constraint is not realistic, and that the difference between the C(C)-C(D) and C(D)-C(E) bonds found earlier is highly significant.

Conclusion

From our statistical tests we have found no evidence of deviation from either the rigid-body thermal motion model or the full-molecular-symmetry model. We have not attempted to fit the third or fourth cumulants introduced by Johnson (1969) but to the approximation of second cumulants (the usual approximation) we should have optimized our molecular geometry determination by applying these physically reasonable constraints. Indeed, we see that the standard deviations for the positional parameters are considerably diminished by the symmetry constraint, giving bond lengths and angles with errors as shown in Fig. 1. An attempt to simplify the model further gave a significantly poorer fit, indicating that the C-C bonds differ significantly in length.

We have presented three different constrained refinements specifically to answer three separate questions. The task of combining these constraint procedures in one general program is great indeed, but a system where this is possible should be aimed at. In the present example the symmetry constraint gave the least change in the R value, the symmetry information being incorporated in the SFLS refinement. This is in contrast to the recent work of Maslen (1968) where this assumed symmetry information is used in 'phase refinement' after the fitting procedure is concluded. It will be of interest to investigate the 'phase refinement' by the use of the results of a symmetry constrained refinement.

We wish to thank Dr John Sherwood of Strathclyde University for growing the crystal, Mr George Paul for help in collecting the diffraction data, and the SRC for the award of a research studentship to one of us (E.A.Y.). Finally we wish to thank Professor W. Cochran for his continued interest in this work.

References

- COOPER, M. J. & ROUSE, K. D. (1968). Acta Cryst. A 24, 405.
- CRUICKSHANK, D. W. J. (1957). Acta Cryst. 10, 504.
- JOHNSON, C. K. (1969). To be published.
- MASLEN, E. N. (1968). Acta Cryst. B24, 1165.
- PAWLEY, G. S. (1964). Acta Cryst. 17, 457.
- PAWLEY, G. S. (1966). Acta Cryst. 20, 631.
- PAWLEY, G. S. (1967). Phys. Stat. Sol. 20, 347.
- PAWLEY, G. S. (1969). Acta Cryst. A25, 531.
- SHERWOOD, J. N. & THOMSON, S. J. (1960). J. Sci. Instrum. 37, 242.

Acta Cryst. (1969). B25, 2013

The Structure of Bis-π-cyclopentadienyl(toluene-3,4-dithiolato)molybdenum

By J.R. KNOX* AND C.K. PROUT

Chemical Crystallography Laboratory, South Parks Road, Oxford, England

(Received 11 November 1968)

 $(\pi$ -C₅H₅)₂MoS₂C₆H₃CH₃ crystallizes in space group $P_{2_1/n}$ with $a=14.97\pm0.01$, $b=17.69\pm0.01$, $c=12.63\pm0.01$ Å, $\beta=115.5\pm0.2^{\circ}$ and Z=8. One of the two molecules is disordered as a result of the presence of both enantiomers in the same site. The least-squares refinement with isotropic temperature factors gave an R value of 0.098 for 3549 observed photographic data. The coordination symmetry about molybdenum approximates to C_{2v} ; the dithiol plane nearly bisects the 132.5° angle between normals to cyclopentadienyl rings, which have a staggered configuration. The average Mo-S distance in the ordered molecule is 2.433\pm0.005 Å.

Introduction

In a molecular orbital description of $(\pi$ -C₅H₅)₂MX₂ compounds Ballhausen & Dahl (1961) suggested that the lone pair of electrons lies between the two bonding

orbitals in a plane between the cyclopentadienyl rings. Their belief that the rings need not be parallel was verified by the structure determination of $(\pi$ -C₅H₅)₂MoH₂ (Gerloch & Mason, 1965), but the angle between Mo-H bonds was not firmly established (Abrahams & Ginsberg, 1966). To clarify the geometry of these compound we determined the structure of bis- π -cyclopendadienyl-(toluene-3,4-dithiolato)molybdenum:

^{*} Present address: Department of Molecular Biophysics, Yale University, New Haven, Conn., U.S.A.



Prior to a preliminary report (Knox & Prout, 1967), Alcock (1967) put forward a modified bonding scheme to explain a departure from the Ballhausen–Dahl bond angle in $C_5H_5(C_5H_5CH_3)Re(CH_3)_2$.

Experimental

Red air-stable crystals were prepared by M.L.H. Green and W.E.Lindsell of the Inorganic Chemistry Laboratory. Cell dimensions were calibrated with aluminum powder lines (a=4.048 Å) superposed on Weissenberg photographs. The crystal data are: MoS₂C₁₇H₁₆, M=380.4, F(000)=1536. Monoclinic, $a=14.97\pm0.01$, $b=17.69\pm0.01$, $c=12.63\pm0.01$ Å, $\beta=115.5\pm0.2^{\circ}$. $D_m=1.685$ g.cm⁻³ (by flotation), Z=8, $D_c=1.705$ g.cm⁻³. Cu K α radiation, $\lambda=1.5418$ Å, $\mu=98$ cm⁻¹. Systematic extinctions: h+l=2n+1 for hol, k=2n+1 for 0k0. Space group: P2₁/n [C⁵_{2h} No. 14.

Table 1.	Fractional	atomic	coordinates	(×	104)	and isotropic	temperature	factors	(×	104	9
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Standrad deviations are given in parentheses. Ordered molecule

	x	y	Z	$U(Å^2)$
Mo(2)	5439 (0.8)	2901 (0.5)	2876 (1.0)	271 (3)
S(3)	5120 (3)	2081(2)	4224 (4)	402 (9)
S(4)	4526 (3)	1924(2)	1474(4)	402(9)
$\tilde{C}(18)$	3559 (10)	0129(8)	3365 (14)	370 3(2)
C(19)	4141 (11)	0723(8)	4005 (14)	381 (33)
C(20)	4430 (10)	1291 (7)	3416(12)	318 (20)
C(21)	4148 (9)	1236(7)	2210(12)	310(29)
C(22)	3549 (11)	1230(7)	1583(14)	A26 (36)
C(23)	3243(12)	0.042(0)	2174(15)	450 (37)
C(24)	3233 (14)	-0485(10)	4006 (17)	430 (37) 507 (48)
C(25)	6710(14)	2220(10)	2500 (17)	563 (40)
C(26)	6052 (16)	2220(10) 2231(12)	2333 (17)	701 (57)
C(27)	7096 (13)	2231(12)	3709 (20) 4217 (16)	512(37)
C(28)	6017 (14)	2372(3) 2454(11)	4217(10) 2214(17)	502 (41)
C(20)	6627 (14)	2050 (11)	3214(17) 3102(17)	592 (47)
C(29)	4450 (15)	2930 (10)	2193(17) 2421(19)	501(45)
C(30)	2001 (14)	3703(11)	3431(10)	505 (51)
C(31)	3001 (14)	3347 (11)	2348 (17)	586 (47)
C(32)	4215 (13)	3624 (10)	1558 (16)	524 (42)
C(33)	4968 (13)	4111 (10)	2081 (16)	518 (41)
C(34)	5154 (14)	4156 (11)	3252 (18)	617 (49)
		Disordered molecu	le	
Mo(1)	5401 (0.9)	3028 (0.6)	7873 (1.2)	375 (4)
S(1a)	4776 (6)	3771 (4)	9031 (9)	330 (11)
S(1b)	4922 (6)	3920 (4)	9028 (9)	334 (11)
S(2a)	4028 (7)	3567 (4)	6238 (10)	386 (12)
S(2b)	4074 (7)	3754 (4)	6280 (10)	383 (12)
C(1 <i>a</i>)	2074 (16)	4806 (17)	7574 (20)	397 (51)
C(1b)	2271 (16)	4935 (18)	7920 (20)	443 (53)
C(2a)	3030 (17)	4572 (22)	8402 (18)	436 (49)
C(2b)	3191 (17)	4626 (23)	8649 (18)	452 (49)
C(3a)	3625 (13)	4161 (14)	8001 (14)	291 (39)
C(3b)	3744 (13)	4283 (15)	8140 (14)	298 (39)
C(4a)	3324 (16)	4065 (18)	6799 (14)	320 (39)
C(4b)	3336 (15)	4172 (19)	6914 (14)	321 (39)
C(5a)	2400 (18)	4350 (23)	5994 (18)	438 (48)
C(5b)	2388 (17)	4443 (23)	6221 (18)	430 (48)
C(6a)	1778 (16)	4698 (17)	6422 (19)	379 (48)
C(6b)	1844 (16)	4832 (17)	6743 (20)	382 (48)
C(7a)	1416 (22)	5195 (20)	8089 (29)	596 (93)
C(7b)	0760 (18)	5068 (20)	6019 (28)	591 (92)
C(8)	6718 (22)	2925 (16)	7342 (28)	1044 (87)
C(9)	7130 (19)	2944 (14)	8525 (24)	860 (70)
C(10)	6915 (15)	3605 (12)	8938 (19)	672 (53)
C(11)	6360 (17)	4034 (13)	7980 (21)	757 (59)
C(12)	6253 (22)	3625 (18)	6974 (26)	1101 (91)
C(12)	6253 (22)	3625 (18)	6974 (26)	1101 (91)
C(14)	4064 (16)	2196 (12)	7404 (20)	688 (54)
C(15)	4726 (20)	1910 (14)	7023 (23)	882 (71)
C(16)	5613 (19)	1746 (15)	7966 (23)	907 (72)
C(17)	5471 (17)	1975 (12)	8957 (21)	743 (60)

Table 2. Observed structure amplitudes and calculated structure factors (electrons)

Each hk column contains l, F_o and F_c . Reflexions marked * were omitted from refinement.

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 $\pm (x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)]$. The tungsten compound is isomorphous.

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From a prismatic crystal measuring $0.1 \times 0.1 \times 0.6$ mm 3314 non-zero hk0 to hk8 reflexions were obtained by the equi-inclination Weissenberg method and were estimated visually. Corrections were made for spot shape variation (Phillips, 1956) and Lorentz-polarization effects, but not for absorption. A second crystal $0.13 \times 0.09 \times 0.17$ mm gave 734 h0l to h2l reflexions

ing produced 3553 independent observable reflexions, and the merging R value, $\Sigma |F_1^2 - F_2^2| / \Sigma |F_1^2 + F_2^2|$, was 0.084.

Solution and refinement of the structure

There are two molecules in the asymmetric unit. As the molybdenum atoms are separated by about $\frac{1}{2}$ along

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z and have nearly the same x and y coordinates, there are two solutions to the Mo-Mo vector set which differ by a shift of $\frac{1}{4}$ along z. Only one set of positions produced a trial structure with acceptable intermolecular distances. In the refinement the quantity minimized was $\Sigma w(F_o - F_c)^2$, where w was initially unity and finally $\{1 + [(|F_o| - a)/b]^2\}^{-1}$ with a = 49 and b = 24 electrons. Scattering curves were taken from International Tables for X-ray Crystallography (1962); the curve for neutral

Mo was corrected for the real part of the dispersion effect ($\Delta f' = -0.5$ e). Hydrogen atoms were not included in structure factor calculations. Unobserved reflexions were omitted from the refinement, as were four strong reflexions 002, 200, $20\overline{2}$, and $2\overline{22}$. Preliminary refinement of only Mo and S parameters gave an R value $\Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.134$ but Fourier syntheses revealed that the methyl group on the dithiol toluene ring in one of the two molecules had only half the expected

Table 5. Intera	tomic aistances (A	A, $\sigma \times 10^3$) and angles (deg, σ	$f \times 10)$		
Ordered mole	cule	Disordered molecule			
$\begin{array}{l} Mo(2)-S(3)\\ Mo(2)-S(4)\\ Mo(2)-C(25)\\ Mo(2)-C(26)\\ Mo(2)-C(27)\\ Mo(2)-C(28)\\ Mo(2)-C(29)\\ Mo(2)-C(30)\\ Mo(2)-C(31)\\ Mo(2)-C(31)\\ Mo(2)-C(33)\\ Mo(2)-C(33)\\ Mo(2)-C(34) \end{array}$	2·434 (5) 2·431 (5) 2·401 (22) 2·368 (25) 2·329 (21) 2·366 (22) 2·302 (22) 2·305 (23) 2·274 (22) 2·267 (20) 2·341 (21) 2·349 (23)	$\begin{array}{c} Mo(1)-S(1a)\\ Mo(1)-S(2a)\\ Mo(1)-S(1b)\\ Mo(1)-S(2b)\\ Mo(1)-C(8)\\ Mo(1)-C(9)\\ Mo(1)-C(10)\\ Mo(1)-C(11)\\ Mo(1)-C(12)\\ Mo(1)-C(13)\\ Mo(1)-C(14)\\ Mo(1)-C(15)\\ Mo(1)-C(16)\\ Mo(1)-C(17)\\ \end{array}$	2:432 (11) 2:396 (13) 2:455 (11) 2:455 (11) 2:346 (35) 2:359 (30) 2:316 (24) 2:253 (26) 2:297 (33) 2:364 (30) 2:364 (30) 2:371 (25) 2:271 (29) 2:287 (29) 2:287 (26)		
Mo(2)-S(3)—C(20) Mo(2)-S(4)—C(21) S(3)—Mo(2)-S(4)	107·9 (6) 108·3 (6) 82·4 (2)	$\begin{array}{l} Mo(1)-S(1a)-C(3a)\\ Mo(1)-S(2a)-C(4a)\\ Mo(1)-S(1b)-C(3b)\\ Mo(1)-S(2b)-C(4b)\\ S(1a)-Mo(1)-S(2a)\\ S(1b)-Mo(1)-S(2b) \end{array}$	105·7 (10) 107·2 (12) 109·0 (10) 106·6 (12) 83·9 (4) 79·2 (4)		
	Ordered toluend	e-3,4-dithiol ligand			
$\begin{array}{l} S(3) & -C(20) \\ S(4) & -C(21) \\ C(18) - C(19) \\ C(19) - C(20) \\ C(20) - C(21) \\ C(21) - C(22) \\ C(22) - C(23) \\ C(23) - C(18) \\ C(18) - C(24) \end{array}$	1.777 (16) 1.766 (16) 1.396 (24) 1.410 (24) 1.399 (22) 1.388 (24) 1.418 (26) 1.371 (25) 1.554 (27)	$\begin{array}{c} S(3) &C(20) - C(19) \\ S(3) &C(20) - C(21) \\ S(4) &C(21) - C(20) \\ S(4) &C(21) - C(22) \\ C(18) - C(19) - C(20) \\ C(19) - C(20) - C(21) \\ C(20) - C(21) - C(22) \\ C(21) - C(22) - C(23) \\ C(22) - C(23) - C(18) \\ C(23) - C(18) - C(24) \\ C(19) - C(18) - C(24) \\ \end{array}$	$\begin{array}{c} 118 \cdot 8 \ (12) \\ 120 \cdot 6 \ (12) \\ 120 \cdot 7 \ (12) \\ 119 \cdot 8 \ (13) \\ 119 \cdot 1 \ (16) \\ 120 \cdot 6 \ (15) \\ 119 \cdot 5 \ (15) \\ 119 \cdot 8 \ (16) \\ 120 \cdot 4 \ (17) \\ 120 \cdot 0 \ (16) \\ 119 \cdot 4 \ (16) \end{array}$		
Cyclopenta	adienyl ligands in o	rdered and disordered molecules			
$\begin{array}{c} C(25)-C(26)\\ C(26)-C(27)\\ C(27)-C(28)\\ C(28)-C(29)\\ C(29)-C(25)\\ C(30)-C(31)\\ C(31)-C(32)\\ C(32)-C(33)\\ C(32)-C(33)\\ C(33)-C(34)\\ C(34)-C(30) \end{array}$	1.362 (34) 1.408 (33) 1.454 (30) 1.472 (31) 1.377 (31) 1.415 (32) 1.384 (30) 1.344 (29) 1.385 (31) 1.404 (32)	$\begin{array}{c} C(8) C(9) \\ C(9) C(10) \\ C(10) - C(11) \\ C(11) - C(12) \\ C(12) - C(8) \\ C(13) - C(14) \\ C(14) - C(15) \\ C(15) - C(16) \\ C(16) - C(17) \\ C(17) - C(13) \end{array}$	$\begin{array}{c} 1\cdot 350 \ (46) \\ 1\cdot 374 \ (38) \\ 1\cdot 365 \ (35) \\ 1\cdot 410 \ (43) \\ 1\cdot 377 \ (48) \\ 1\cdot 271 \ (39) \\ 1\cdot 372 \ (39) \\ 1\cdot 380 \ (41) \\ 1\cdot 416 \ (39) \\ 1\cdot 356 \ (40) \end{array}$		
$\begin{array}{c} C(29)-C(25)-C(26)\\ C(25)-C(26)-C(27)\\ C(26)-C(27)-C(28)\\ C(27)-C(28)-C(29)\\ C(28)-C(29)-C(25)\\ C(34)-C(30)-C(31)\\ C(30)-C(31)-C(32) \end{array}$	109·4 (20) 111·8 (21) 104·9 (19) 106·5 (18) 107·2 (19) 106·7 (20) 106·1 (19)	$\begin{array}{c} C(12)-C(8)-C(9)\\ C(8)-C(9)-C(10)\\ C(9)-C(10)-C(11)\\ C(10)-C(11)-C(12)\\ C(11)-C(12)-C(8)\\ C(17)-C(13)-C(14)\\ C(13)-C(14)-C(15) \end{array}$	105.8 (30) 111.8 (27) 106.8 (23) 107.6 (24) 107.9 (28) 114.5 (27) 105.7 (25)		

111.1 (19)

107.6 (19)

108.4 (20)

C(30) - C(31) - C(32)C(31)-C(32)-C(33)

C(32) - C(33) - C(34)

C(33)-C(34)-C(30)

C(14)-C(15)-C(16)

C(15)-C(16)-C(17)

C(16)-C(17)-C(13)

110.3 (26)

104.4 (25)

104.8 (24)

Table 3 Interatornia distances (Å $\sigma \times 103$ and analog (dog $\sigma \times 10$) peak height and that a second peak was appearing 1.5 Å from the adjacent ring carbon atom. The adjoining ring distance was 1.23 Å.

The suspected disorder in the dithiol toluene ring was dealt with by imposing a semi-rigid configuration on each of two overlapping toluene rings a and b (see Fig. 1). The two initial sets of coordinates were obtained by positioning a template on a map grid calculated in the ligand plane. The dimensions of the template were taken from the chemically-similar ordered molecule. A matching of methyl and sulphur template positions with the corresponding peaks in the map sufficiently defined the coordinates of ring carbon atoms. The positional parameters of the 18 dithiol atoms *ia* and *ib* were grouped together in one matrix block. Their occupation numbers were held constant at 0.5.

In a conditional refinement (Waser, 1963) programmed by G. Ford and J.S. Rollett, who will publish details of the method at a later date, the function minimized was $\Sigma w(F_o - F_c)^2 + \Sigma w'(d - d')^2 + \Sigma w''(U_{ia} - U_{ib})^2$. The d are bonded and non-bonded distances in the disordered dithiol configurations a and b, and the d'are template distances. The temperature factor condition $U_{ia} = U_{ib}$ was introduced because at each peak position (except methyl group positions) there are two halfatoms ia and ib. The weights w' and w'' were of the order $1/\sigma_d^2$, and $1/\sigma_u^2$; they were adjusted slightly during refinement until the desired fit of d with d' and U_{ia} with U_{ib} was obtained. Each distance and temperature factor was therefore treated as an additional observation. After four cycles the rate of convergence of parameter shifts was increased by the application of appropriate relaxation factors calculated for a five-cycle accelerated block-diagonal refinement (Hodgson & Rollett, 1963). An additional cycle with a relaxation factor of 1.0gave shifts less than 0.13 of their estimated standard deviations. The final atomic coordinates and isotropic temperature factors (Table 1) gave an R value of 0.098 for 3549 observed reflexions (Table 2). The weighting scheme satisfactorily held distances in each dithiol ring a and b to within 1σ of those in the ordered ring (Table 3) and kept U_{ia} within 1σ of U_{ib} . The weights w' for d(C-S) were $1/(0.020)^2$, for d(C-C ring), $1/(0.035)^2$ and for $d(C-CH_3) 1/(0.040)^2$. The w'' were $1/(0.0011)^2$ for sulphur atoms and $1/(0.0055)^2$ for carbon atoms. Final positions for dithiol atoms are plotted in Fig.1. The greates separation of the two semi-rigid configurations is 0.47 Å and occurs in the diffuse peaks farthest from molybdenum.

The disordered species is a superposition of one molecule with its enantiomer, and not a superposition with itself through a 180° rotation.



Fourier sections through the cyclopentadienyl rings of the disordered molecule showed only five electron-density peaks and not ten half-weight peaks. Each peak then contains two closely spaced half-carbon atoms, to which it was practicable to assign only one set of coordinates. Consequently temperature factors of atoms C(8) to C(17) and of Mo(1) are 50% higher than those



Fig.1. Electron density sections through disordered and ordered toluene-3,4-dithiolate ligands. Contour intervals are 1, 2, 4, 6 e.Å⁻³ for carbon, and 2, 4, 8, 12, 16, 20 e.Å⁻³ for sulphur.

of C(25) to C(34) and Mo(2) in the ordered molecule. The asymmetric unit of the cell contains more of one enantiomer than the other by a ratio of 3/2 to $\frac{1}{2}$. However, the space group inversion centre ensures that the crystal contains equal numbers of each enantiomer.

Discussion

The 82.4° angle between Mo–S bonds in the undisordered molecule is considerably less than the 150° value derived by Ballhausen & Dahl (1961). It is unlikely that the lone pair of electrons is able to occupy the third orbital which, according to theory, would in this case be directed into the chelate ring. A better bonding scheme for this compound is the one derived by Alcock (1967) to account for the 76° angle in $C_5H_5(C_5H_5CH_3)Re(CH_3)_2$. Any π -character in the Mo–S bonds is probably not a result of electron delocalization in the planar chelate ring, as the average distance, 2.433 Å, is equal to the 2.438 Å distance in the nonplanar saturated ring in $(\pi-C_5H_5)_2MoS(CH_2)_2NH_2^+I^-$ (Knox & Prout, 1969).

The coordination symmetry of the Mo-S bonds and ring normals approximates to C_{2v} , but is strictly only C_1 . The normal to the S-Mo-S plane is perpendicular (88.8°) to the normal of the plane of the two ring normals. But the Mo-S(3) and Mo-S(4) bonds are unequally inclined to the plane of the ring normals (37.4°, cf. 44.9°, $\sigma = 1.5$), and the ring normals make unequal angles with the S-Mo-S plane, 63.4° for ring C(25-29), cf. 69.0° for ring C(30-34). Ring normals have no Cs symmetry across the S-Mo-S plane because the ring C(30-34) meets the sulphur atom not at the frontal C(31) atom but at the two carbon atoms farther back, and the ring normal moves forward by 5.6° until both C...S contacts are 3.05 Å, equal to the contacts made by the second ring.

In a comprehensive review Wheatley (1967) suggests that whether two rings are staggered or eclipsed is largely independent of any intramolecular forces, and cites $(\pi$ -C₅H₅)₂MoH₂ (Gerloch & Mason, 1965) as having an eclipsed configuration even though the distance between the nearest pair of carbon atoms is 3.07 Å. In the present molecule nearest distances are even smaller, being 2.88 and 2.94 Å from C(28) to staggered atoms C(33) and C(34). Hypothetically, if the rings were eclipsed and the angle between ring normals unchanged, the separation would be only 2.74 Å. Clearly, the intramolecular forces resulting from the crowding between sulphur atoms and cyclopentadienyl rings and between carbon atoms of each, ring produce not only the staggered configuration but also an angle between ring normals which is much smaller (132.5°) than the 146° angle in $(\pi$ -C₅H₅)₂MoH₂ and is the edge of the 135–180° range permitted by the Ballhausen & Dahl scheme. On either steric or electronic grounds the molybdenum-to-plane distance should be longer in this dithiol molecule, though perhaps not measurable



Fig.2. Relative configuration of cyclopentadienyl rings and sulphur atoms about molybdenum in the ordered molecule.

There is, in fact, an increase (0.06 Å) but it is less than 3σ.

There is no recognizable pattern of asymmetry in the C-C bond distances in the cyclopentadienyl rings. Furthermore, the 3σ variation in the C(25-29) distances is not likely to be real, as the standard deviations from the block-diagonal refinement are probably under estimated. The variation in the Mo-C distances to the C(25–29) ring is 5σ , and the distances have the relationship Mo-C(28) < Mo-C(27) = Mo-C(29) < Mo-C(25)= Mo-C(26), the longest pair of distances being above the two sulphur atoms (Fig. 2). It is not clear why this equality of Mo-C distances across a vertical plane bisecting the chelate angle is not seen in the second ring C(30-34). Possibly the approach of $CH_3(24)$ to C(31)and C(32) (Fig. 3) is tilting the ring so that Mo-C(30)differs from Mo–C(32) by 4σ .

The dimensions of the dithiol ligand in the ordered molecule are similar to those in the bis(toluene-3,4dithiolato)cobalt anion (Eisenberg, Dori, Gray & Ibers, 1968). Atoms in the ligand are within 0.05 Å of the least-squares plane (Table 4), which is inclined only 2.6° to the S-Mo-S plane.

Table 4. Least-squares planes in ordered molecule Distances (Å) of atoms from plane

(Parentheses denote atoms not in calculation.)

	1	2	3	4
Mo(2)	-0.009	(-0.073)	(-1.999)	(-1.993)
S(3)	0.003	<u></u> -0.051	(()
S(4)	0.017	0.036		
C(18)	(-0.054)	0.012		
C(19)	(0.004)	0.025		
C(20)	0.011	0.012		
C(21)	-0.025	0.016		
C(22)	(-0.112)	-0.027		
C(23)	(-0.147)	-0.048		
C(24)	(-0.070)	0.016		
C(25)			0.018	



Fig. 3. Projection down z. Atoms in the disordered molecule have been transformed to $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

Table 4 (cont.)							
	1	2	3	4			
C(26)			-0.008				
C(27)			-0.006				
C(28)			0.016				
C(29)			-0.021				
C(30)				0.019			
C(31)				-0.013			
C(32)				0.002			
C(33)				0.010			
C(34)			:	-0.018			
Equ	ations of pla	anes. $lX + m$	Y + nZ = p				
with X=	$=xa+zc\cos b$	β , $Y = yb$ and	nd $Z = zc \sin \beta$	•			
1	0.8435	-0.4978	0.2020	3.666			
2	0.8341	-0.5217	0.1791	3.472			
3	0.9819	-0.0492	0.1827	8.806			
4	-0.6020	0.7610	-0.2290	1.154			
Mo(2)S(3)S(4)	0.8478	0.4884	0.2066	3.749			
C_5H_5 normals	-0.1732	0.1546	0.9727	2.843			

We wish to thank the National Institute of General

Medical Sciences, U.S. Public Health Service, for a

fellowship to J.R.K. Calculations were done on the

Oxford University KDF9 computer with the NOVTAPE

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programs developed by J. H. Holbrook, J. S. Rollett and B. R. Stonebridge and modified by O. J. R. Hodder. The conditional refinement was programmed by G. Ford.

References

ABRAHAMS, S. C. & GINSBERG, A. P. (1966). *Inorg. Chem.* 5, 500.

ALCOCK, N. W. (1967). J. Chem. Soc. A, p. 2001.

- BALLHAUSEN, C. J. & DAHL, J. P. (1961). Acta Chem. Scand. 15, 1333.
- EISENBERG, R., DORI, Z., GRAY, H. B. & IBERS, J. A. (1968). Inorg. Chem. 7, 741.
- GERLOCH, M. & MASON, R. (1965). J. Chem. Soc. p. 296.
- HODGSON, L. I. & ROLLETT, J. S. (1963). Acta Cryst. 16, 329.
- International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 211. Birmingham: Kynoch Press.
- KNOX, J. R. & PROUT, C. K. (1967). Chem. Comm. p. 1277.
- KNOX, J. R. & PROUT, C. K. (1969). Acta Cryst. To be published.

PHILLIPS, D. C. (1956). Acta Cryst. 9, 819.

WASER, J. (1963). Acta Cryst. 16, 1091.

WHEATLEY, P. J. (1967). In Perspectives in Structural Chemistry, Ed. J. D. DUNITZ & J. A. IBERS. Vol. I, p. 1. London: Wiley.

Acta Cryst. (1969). B25, 2022

The Crystal and Molecular Structure of Octa-cis-2, trans-6-diene-1,8-dioic Acid

By Ezio Martuscelli

Laboratorio di Ricerche su Tecnologia dei Polimeri e Reologia del C.N.R., c/o Istituto Chimico dell'Università di Napoli, Via Mezzocannone 4, 80134 Napoli, Italy

and Lelio Mazzarella

Istituto di Chimica Fisica, c/o Istituto Chimico dell'Università di Napoli, Via Mezzocannone 4,80134 Napoli, Italy

(Received 18 November 1968)

The crystal structure of octa-cis-2,trans-6-diene-1,8-dioic acid, $C_8O_4H_{10}$, has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the centrosymmetric monoclinic space group P_{21}/c . The unit cell contains four molecules and has the dimensions $a = 7.75 \pm 0.02$, $b = 17.34 \pm 0.03$, $c = 10.10 \pm 0.02$ Å; $\beta = 138^{\circ}52' \pm 30'$. The molecules are associated in rows in the crystal lattice. The molecular rows lie in planes parallel to (101), alternately oriented along the a+b+c and a-b+c crystallographic directions. The values of the rotation angles around the single bonds C(5)–C(6) and C(3)–C(4) adjacent to the double bond in *trans* configuration and to the double bond in *cis* configuration are 126.6° and -97° respectively.

Introduction

The determination of the crystal and molecular structure of octa-cis-2, trans-6-diene-1, 8-dioic acid,



is part of a research programme whose aim is the determination of the values of internal rotation angles about single bonds adjacent to double bonds. As model compounds a series of aliphatic unsaturated bicarboxylic acids have been studied (Ganis & Martuscelli, 1966; Martuscelli, 1967). In fact, though the problem of hindered rotation around single bonds adjacent to double bonds has been extensively studied on simple molecules in the vapour and liquid phases by spectroscopic techniques (nuclear magnetic resonance, microwave and Raman spectroscopy; electron diffraction), only a few values of the conformational parameters determined by X-ray methods in the solid state are to be found in the literature.

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