

A constrained refinement was carried out, giving $C-C=1.4056 \pm 0.0015 \text{ \AA}$ and $C-D=1.073 \pm 0.003 \text{ \AA}$, 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.

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

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(Received 11 November 1968)

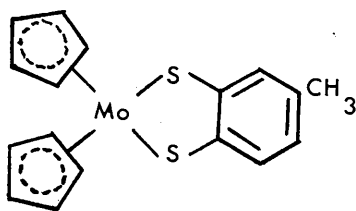
$(\pi-C_5H_5)_2MoS_2C_6H_3CH_3$ crystallizes in space group $P2_1/n$ with $a=14.97 \pm 0.01$, $b=17.69 \pm 0.01$, $c=12.63 \pm 0.01 \text{ \AA}$, $\beta=115.5 \pm 0.2^\circ$ and $Z=8$. One of the two molecules is disordered as a result of the presence of both enantiomers in the same site. The least-squares 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 $2.433 \pm 0.005 \text{ \AA}$.

Introduction

In a molecular orbital description of $(\pi-C_5H_5)_2MX_2$ 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 $(\pi-C_5H_5)_2MoH_2$ (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 -cyclopentadienyl-(toluene-3,4-dithiolato)molybdenum:

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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 ($a=4.048 \text{ \AA}$) superposed on Weissenberg photographs. The crystal data are: $MoS_2C_{17}H_{16}$, $M=380.4$, $F(000)=1536$. Monoclinic, $a=14.97 \pm 0.01$, $b=17.69 \pm 0.01$, $c=12.63 \pm 0.01 \text{ \AA}$, $\beta=115.5 \pm 0.2^\circ$. $D_m=1.685 \text{ g.cm}^{-3}$ (by flotation), $Z=8$, $D_c=1.705 \text{ g.cm}^{-3}$. Cu $K\alpha$ radiation, $\lambda=1.5418 \text{ \AA}$, $\mu=98 \text{ cm}^{-1}$. Systematic extinctions: $h+l=2n+1$ for $h0l$, $k=2n+1$ for $0k0$. Space group: $P2_1/n [C_{2h}^5 \text{ No. } 14]$.

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^4$)

Standard deviations are given in parentheses.

	x	y	z	$U(\text{\AA}^2)$
Ordered molecule				
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)	419 (9)
C(18)	3559 (10)	0129 (8)	3365 (14)	370 3(2)
C(19)	4141 (11)	0733 (8)	4005 (14)	381 (33)
C(20)	4430 (10)	1291 (7)	3416 (12)	318 (29)
C(21)	4148 (9)	1236 (7)	2210 (12)	319 (29)
C(22)	3549 (11)	0642 (8)	1583 (14)	426 (36)
C(23)	3243 (12)	0091 (9)	2174 (15)	450 (37)
C(24)	3233 (14)	-0485 (10)	4006 (17)	597 (48)
C(25)	6710 (14)	2220 (10)	2599 (17)	563 (44)
C(26)	6952 (16)	2231 (12)	3769 (20)	721 (57)
C(27)	7096 (13)	2972 (9)	4217 (16)	512 (41)
C(28)	6917 (14)	3454 (11)	3214 (17)	592 (47)
C(29)	6637 (13)	2950 (10)	2193 (17)	561 (45)
C(30)	4459 (15)	3705 (11)	3431 (18)	655 (51)
C(31)	3881 (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 molecule				
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(1a)	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 I , F_o and F_c . Reflexions marked * were omitted from refinement.

h	k	l	I	F _o	F _c
0	0	0	4000	4000	4000
0	0	1	100	100	100
0	0	2	200	200	200
0	0	3	300	300	300
0	0	4	400	400	400
0	0	5	500	500	500
0	0	6	600	600	600
0	0	7	700	700	700
0	0	8	800	800	800
0	0	9	900	900	900
0	0	10	1000	1000	1000
0	0	11	1100	1100	1100
0	0	12	1200	1200	1200
0	0	13	1300	1300	1300
0	0	14	1400	1400	1400
0	0	15	1500	1500	1500
0	0	16	1600	1600	1600
0	0	17	1700	1700	1700
0	0	18	1800	1800	1800
0	0	19	1900	1900	1900
0	0	20	2000	2000	2000
0	0	21	2100	2100	2100
0	0	22	2200	2200	2200
0	0	23	2300	2300	2300
0	0	24	2400	2400	2400
0	0	25	2500	2500	2500
0	0	26	2600	2600	2600
0	0	27	2700	2700	2700
0	0	28	2800	2800	2800
0	0	29	2900	2900	2900
0	0	30	3000	3000	3000
0	0	31	3100	3100	3100
0	0	32	3200	3200	3200
0	0	33	3300	3300	3300
0	0	34	3400	3400	3400
0	0	35	3500	3500	3500
0	0	36	3600	3600	3600
0	0	37	3700	3700	3700
0	0	38	3800	3800	3800
0	0	39	3900	3900	3900
0	0	40	4000	4000	4000
0	1	0	100	100	100
0	2	0	200	200	200
0	3	0	300	300	300
0	4	0	400	400	400
0	5	0	500	500	500
0	6	0	600	600	600
0	7	0	700	700	700
0	8	0	800	800	800
0	9	0	900	900	900
0	10	0	1000	1000	1000
0	11	0	1100	1100	1100
0	12	0	1200	1200	1200
0	13	0	1300	1300	1300
0	14	0	1400	1400	1400
0	15	0	1500	1500	1500
0	16	0	1600	1600	1600
0	17	0	1700	1700	1700
0	18	0	1800	1800	1800
0	19	0	1900	1900	1900
0	20	0	2000	2000	2000
0	21	0	2100	2100	2100
0	22	0	2200	2200	2200
0	23	0	2300	2300	2300
0	24	0	2400	2400	2400
0	25	0	2500	2500	2500
0	26	0	2600	2600	2600
0	27	0	2700	2700	2700
0	28	0	2800	2800	2800
0	29	0	2900	2900	2900
0	30	0	3000	3000	3000
0	31	0	3100	3100	3100
0	32	0	3200	3200	3200
0	33	0	3300	3300	3300
0	34	0	3400	3400	3400
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0	37	0	3700	3700	3700
0	38	0	3800	3800	3800
0	39	0	3900	3900	3900
0	40	0	4000	4000	4000
1	0	0	100	100	100
2	0	0	200	200	200
3	0	0	300	300	300
4	0	0	400	400	400
5	0	0	500	500	500
6	0	0	600	600	600
7	0	0	700	700	700
8	0	0	800	800	800
9	0	0	900	900	900
10	0	0	1000	1000	1000
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28	0	0	2800	2800	2800
29	0	0	2900	2900	2900
30	0	0	3000	3000	3000
31	0	0	3100	3100	3100
32	0	0	3200	3200	3200
33	0	0	3300	3300	3300
34	0	0	3400	3400	3400
35	0	0	3500	3500	3500
36	0	0	3600	3600	3600
37	0	0	3700	3700	3700
38	0	0	3800	3800	3800
39	0	0	3900	3900	3900
40	0	0	4000	4000	4000
0	1	1	100	100	100
0	2	2	200	200	200
0	3	3	300	300	300
0	4	4	400	400	400
0	5	5	500	500	500
0	6	6	600	600	600
0	7	7	700	700	700
0	8	8	800	800	800
0	9	9	900	900	900
0	10	10	1000	1000	1000
0	11	11	1100	1100	1100
0	12	12	1200	1200	1200
0	13	13	1300	1300	1300
0	14	14	1400	1400	1400
0	15	15	1500	1500	1500
0	16	16	1600	1600	1600
0	17	17	1700	1700	1700
0	18	18	1800	1800	1800
0	19	19	1900	1900	1900
0	20	20	2000	2000	2000
0	21	21	2100	2100	2100
0	22	22	2200	2200	2200
0	23	23	2300	2300	2300
0	24	24	2400	2400	2400
0	25	25	2500	2500	2500
0	26	26	2600	2600	2600
0	27	27	2700	2700	2700
0	28	28	2800	2800	2800
0	29	29	2900	2900	2900
0	30	30	3000	3000	3000
0	31	31	3100	3100	3100
0	32	32	3200	3200	3200
0	33	33	3300	3300	3300
0	34	34	3400	3400	3400
0	35	35	3500	3500	3500
0	36	36	3600	3600	3600
0	37	37	3700	3700	3700
0	38	38	3800	3800	3800
0	39	39	3900	3900	3900
0	40	40	4000	4000	4000
1	1	1	100	100	100
2	2	2	200	200	200
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9	9	9	900	900	900
10	10	10	1000	1000	1000
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12	12	12	1200	1200	1200
13	13	13	1300	1300	1300
14	14	14	1400	1400	1400
15	15	15	1500	1500	1500
16	16	16	1600	1600	1600
17	17	17	1700	1700	1700
18	18	18	1800	1800	1800
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20	20	20	2000	2000	2000
21	21	21	2100	2100	2100
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23	23	23	2300	2300	2300
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33	33	33	3300	3300	3300
34	34	34	3400	3400	3400
35	35	35	3500	3500	3500
36	36	36	3600	3600	3600
37	37	37	3700	3700	3700
38	38	38	3800	3800	3800
39	39	39	3900	3900	3900
40	40	40	4000	4000	4000

Table 2 (*cont.*)

17	001	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600	610	620	630	640	650	660	670	680	690	700	710	720	730	740	750	760	770	780	790	800	810	820	830	840	850	860	870	880	890	900	910	920	930	940	950	960	970	980	990	1000
17	001	100	110	120	130	140	150	160	170	180	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400	410	420	430	440	450	460	470	480	490	500	510	520	530	540	550	560	570	580	590	600	610	620	630	640	650	660	670	680	690	700	710	720	730	740	750	760	770	780	790	800	810	820	830	840	850	860	870	880	890	900	910	920	930	940	950	960	970	980	990	1000

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

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

which were used for scaling the first data set. Final scaling produced 3553 independent observable reflexions, and the merging R value, $\sum |F_1^2 - F_2^2| / \sum |F_1^2 + F_2^2|$, 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

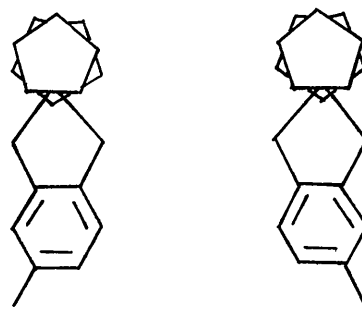
peak height and that a second peak was appearing 1.5 Å from the adjacent ring carbon atom. The adjoining ring distance was 1.23 Å.

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 $\sum w(F_o - F_c)^2 + \sum w'(d - d')^2 + \sum w''(U_{ia} - U_{ib})^2$. 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 half-atoms *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 1.0 gave 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 $d(\text{C-S})$ were $1/(0.020)^2$, for $d(\text{C-C ring})$, $1/(0.035)^2$ and for $d(\text{C-CH}_3)$ $1/(0.040)^2$. 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 greatest 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

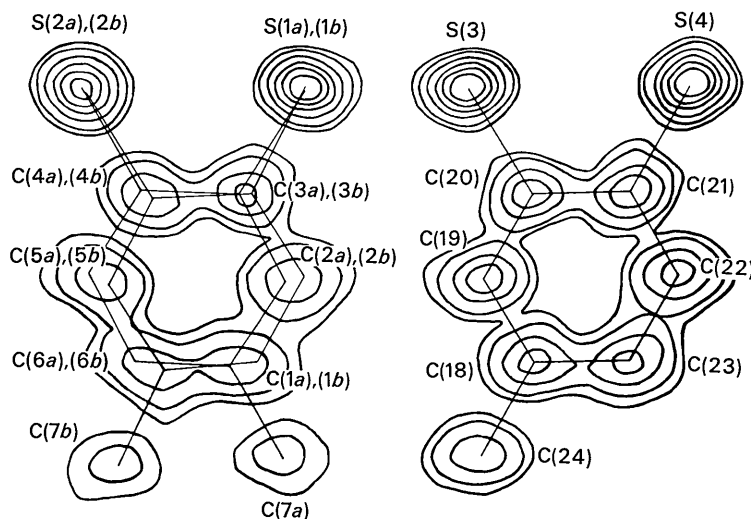


Fig. 1. Electron density sections through disordered and ordered toluene-3,4-dithiolate ligands. Contour intervals are 1, 2, 4, 6 e.Å⁻³ for carbon, and 2, 4, 8, 12, 16, 20 e.Å⁻³ for sulphur.

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 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 un-disordered 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 non-planar 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 C_s 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 $(\pi-C_5H_5)_2MoH_2$ (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 $(\pi-C_5H_5)_2MoH_2$ 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

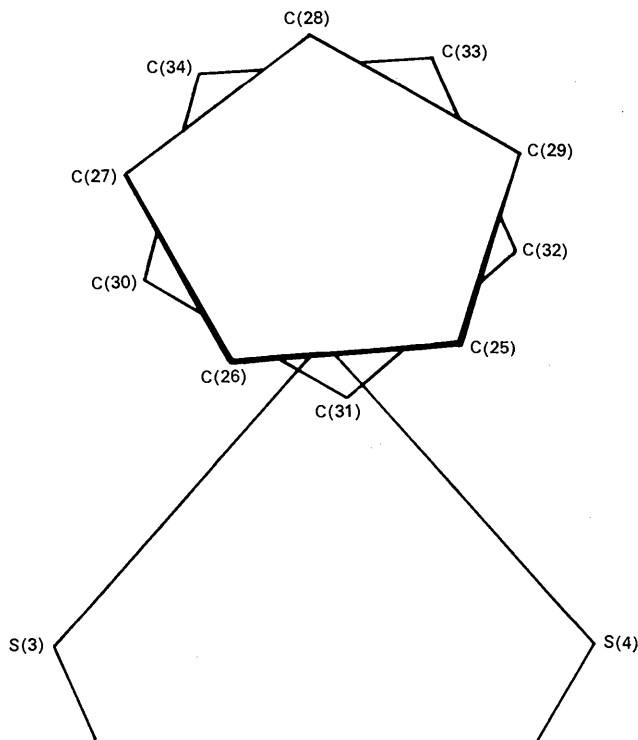


Fig. 2. Relative configuration of cyclopentadienyl rings and sulphur atoms about molybdenum in the ordered molecule.

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 underestimated. 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 CH₃(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(toluenes-3,4-

dithiolato)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	-0.051		
S(4)	0.017	0.036		
C(18)	(-0.054)	0.015		
C(19)	(0.004)	0.025		
C(20)	0.011	0.017		
C(21)	-0.022	0.016		
C(22)	(-0.112)	-0.027		
C(23)	(-0.147)	-0.048		
C(24)	(-0.070)	0.016		
C(25)			0.018	

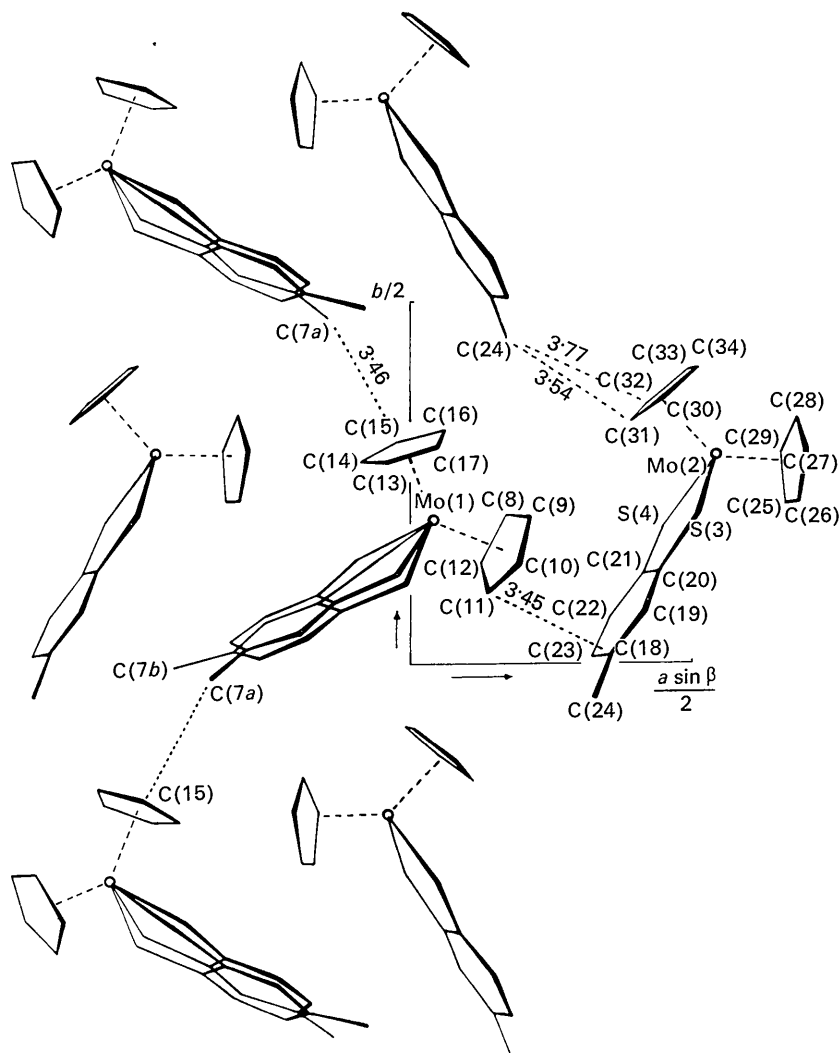


Fig. 3. Projection down z . Atoms in the disordered molecule have been transformed to $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

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

Equations of planes. $lX + mY + nZ = p$
with $X = xa + zc \cos \beta$, $Y = yb$ and $Z = zc \sin \beta$.

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	-0.6070	0.7610	-0.2290	1.154
Mo(2)S(3)S(4)	0.8478	0.4884	0.2066	3.749
C ₅ H 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*

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.

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Acta Cryst. (1969). B25, 2022

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

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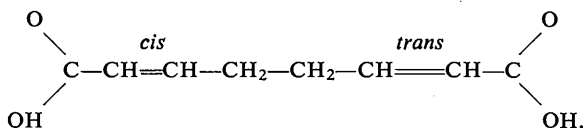
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(Received 18 November 1968)

The crystal structure of octa-*cis*-2,*trans*-6-diene-1,8-dioic acid, C₈O₄H₁₀, has been determined from three-dimensional X-ray diffraction data. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. 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 (10 $\bar{1}$), 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 dicarboxylic 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.