sec-butyl and 5-ethyl-5-(1-methylbutyl) barbituric acids. Crystals of these compounds have been shown to have structures which closely resemble amobarbital II (Craven & Cusatis, unpublished). However, it is unlikely that barbiturates substituted with unbranched chains at C(5) could have a double ribbon structure because the chain packing would be very inefficient. A double ribbon structure is not found in barbital I, II or IV\* (Craven, Vizzini & Rodrigues, 1969). More work is needed to determine the extent to which chain length in a C(5) substituent affects the occurrence of double ribbons in barbiturate crystal structures. It is probable that length is a less critical factor than cross sectional area.

Solid solutions and molecular complex formation have been reported in many binary systems of 5,5'dialkylbarbiturates (Brandstätter-Kuhnert & Vlachopoulos, 1967). This suggests the existence of hydrogen bonded frameworks in the solid state which are not greatly perturbed when one barbiturate is substituted for another. The double ribbon structure is well suited to this role, and in fact occurs in solid solutions in at least one such binary system (amobarbital/vinbarbital; Craven & Cusatis, unpublished).

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\* The crystal structure of barbital IV has not yet been determined, but the lattice translations are incompatible with a double ribbon structure.

assembled and modified by Dr R.Shiono, Crystallography Laboratory, University of Pittsburgh.

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# A Neutron-Diffraction Study of Perdeuteronaphthalene

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The crystal structure of perdeuteronaphthalene,  $C_{10}D_8$ , is very similar to that of  $C_{10}H_8$ . The space group is  $P2_1/a$  with  $a=8.266\pm0.008$ ,  $b=5.968\pm0.006$ ,  $c=8.669\pm0.008$  Å;  $\beta=122.92\pm0.02^{\circ}$ . 331 independent observations give an *R* value of 5.2% in a refinement where the anisotropic temperature factors were fixed at the best values obtained with the use of the rigid-body thermal-motion constraint, and the positional parameters were constrained to the *mmm* symmetry of the free molecule. Statistical tests showed that no significant improvement is possible on removing the constraints. Consequently, the molecular geometry resulting from the constrained refinements was better determined than it would have been from a conventional unconstrained refinement.

### Introduction

The present investigation of the crystal structure of perdeuteronaphthalene,  $C_{10}D_8$ , is part of the study of the lattice dynamics of molecular crystals. Measurement of phonon frequencies is best done with neutron

inelastic coherent scattering. Hydrogen is a very strong incoherent scatterer, and for this reason fully deuterated crystals are preferred.

Calculations have been made of phonon frequencies in naphthalene by Pawley (1967), with the use of the crystal structure of  $C_{10}H_8$  as determined by X-ray diffraction (Cruickshank, 1957). We expected a slight change in crystal structure on deuteration and this we wished to find. Neutron diffraction affords a method of accurate determination of nuclear positions and is ideal for obtaining a starting point for lattice dynamical calculations.

The easiest of these calculations to make involves rigid-body motion of the molecules. Consequently when the diffraction data are used to refine the crystal structure, a structure-factor least-squares (SFLS) procedure incorporating a rigid-body thermal parameter constraint is appropriate (Pawley, 1964). If the assumption of molecular rigidity is valid we would expect the molecules to retain in the crystal the symmetry they have in the free state. Consequently another constrained SFLS refinement is of interest, in which the molecules are kept to *mmm* symmetry in the crystal although the molecular site is only centrosymmetric.

### Experimental

A large single crystal of 98% deuterated naphthalene was grown by Dr Sherwood of the University of Strathclyde by the moving-vessel technique (Sherwood & Thomson, 1960). A sphere of diameter 7 mm was cut from one end of the crystal, and was mounted with  $z^*$  vertical, inside a sealed soda-glass bulb to reduce sublimation losses. The mosaic spread of the crystal was  $0.5^{\circ}$  (full width at half height) which was thought to be sufficient for extinction effects to be small, therefore no shock cooling was attempted. Rapid cooling in liquid nitrogen tends to shatter large crystals of this sort.

The unit cell of  $\tilde{C}_{10}D_8$  is slightly different from that of  $C_{10}H_8$ , being

 $a = 8 \cdot 266 \pm 0.008 \text{ Å}$   $b = 5 \cdot 968 \pm 0.006$   $c = 8 \cdot 669 \pm 0.008 \text{ in } P2_1/a.$  $\beta = 122 \cdot 92 \pm 0.02^{\circ}$ 

331 independent intensities were measured at 295 °K on the Ferranti four-circle diffractometer on the DIDO reactor at Harwell. A number of equivalent reflexion pairs were measured and the average agreement was 1%. Table 1 contains the  $|F_{obs}|$  used in the structure refinements.

### Computational

No attempts were made to correct the data for absorption, extinction or thermal diffuse scattering. The maximum of absorption was 7%, owing mainly to the incoherent scattering from the 2% of hydrogen. The angular variation in absorption would be much smaller than this, giving a slight error to the mean-square translational displacement tensor  $\mathbf{T}$ . We found no evidence of extinction when analysing the result of the refine-

# Table 1. Observed and calculated structure factors

The columns are hkl,  $|F_{obs}|$ ,  $|F^{r.b.}_{calc}|$  and  $|F^{mmm}_{calc}|$ .

a a a ata aat 300	1 2 2 482 401 442	a a -1 fina fina fina	3 3 -7 218 218 224	4 4 5 366 346 343	5 6 -6 195 198 191
0 0 2 353 305 302	1 3 4 770 741 754	2 3 2 618 567 575	3 3 -8 267 278 288	4 4 -6 549 532 503	6 0 -1 583 559 569 6 0 2 175 227 223
0 0 4 1330 1301 1299 0 0 5 357 326 344	1 3 -4 280 290 282	2 3 -2 427 433 440 2 3 3 460 422 441	3 4 -1 225 196 204	4 5 1 488 462 467	6 0 -4 1142 1128 1149
0 0 7 350 289 316	1 3 -5 530 488 501	2 3 4 955 953 958 2 3 5 514 493 473	3 4 2 543 523 541 3 4 -3 567 548 550	4 5 -3 378 388 401	6 1 0 283 298 295
0 1 3 622 588 583	1 4 0 222 229 226	2 3 6 403 360 369	3 4 -5 437 404 426	4 5 -5 475 455 404	6 1 -2 144 122 150 6 1 -4 296 264 267
0 1 4 062 001 038	1 4 -1 598 681 685	2 4 -1 353 349 345	3 4 -7 263 267 275	4 6 -2 310 287 293	6 1 -5 285 280 299
0 1 7 265 225 239	1 4 -2 201 185 181	2 4 2 390 336 336 2 4 -2 634 618 617	3 5 1 004 039 037 3 5 - 2 1001 1018 1014	4 6 -5 319 318 321	6 2 2 145 154 149
0 2 0 739 672 678	1 4 -5 920 956 966	2 4 4 242 223 212	3 5 -3 715 712 729	4 7 0 244 248 244	6 2 -2 716 704 696 6 2 3 172 204 204
0 2 1 482 427 430 0 2 2 958 893 908	1 5 -1 204 208 188 1 5 2 331 332 334	2 4 -5 045 025 020 2 5 0 114 104 106	3 5 -6 571 578 569	4 7 -5 285 285 301	6 2 -3 248 224 255
0 2 6 672 689 691	1 5 -2 564 536 529	2 5 2 322 337 330	37-3140153142 37-6634538	4 7 -6 300 269 300 4 8 2 132 163 157	6 3 0 126 116 108
0 3 1 756 732 728	1 5 5 226 243 253	2 5 3 127 147 160	3 8 -2 147 152 154	4 8 -3 127 129 135	6 3 -1 322 339 338 6 3 -2 404 511 400
0 3 3 000 507 577 0 3 4 321 305 326	1 6 -2 405 409 414 1 6 5 272 240 230	2 5 -4 294 278 290 2 5 5 259 244 238	4 0 1 192 193 183	5 1 1 68 71 70	6 3 -3 536 516 507
0 3 5 497 476 470	1 6 - 5 383 392 398	2 5 -5 336 336 342	4 0 -1 441 405 427 4 0 2 141 168 180	5 1 -1 341 330 339 5 1 2 223 192 197	6 4 0 378 374 377
0 4 2 217 213 210	1 8 1 62 61 56	2 6 2 425 413 415	4 0 -2 502 469 489	5 1 -2 214 202 216	6 4 -3 663 677 671 6 4 4 170 180 177
0 4 4 805 797 808 0 4 5 601 603 589	1 8 -3 214 230 225 2 0 0 1301 1446 1447	2 0 -4 100 179 179 2 6 -6 248 266 256	4 0 -4 263 263 281	5 1 4 284 284 280	6 4 -4 319 323 319
0 5 1 375 366 354	2 0 1 619 575 557	2 7 1 505 528 538	4 0 -5 267 258 268 4 0 6 304 281 298	5 1 -4 585 577 594 5 1 -8 477 412 411	0 5 -2 414 442 430 6 6 -6 551 547 552
0 5 4 50 15 16	2 0 2 474 423 415	2 7 2 420 433 445	4 0 -6 296 309 332	5 1 -9 390 373 373	6 7 -2 102 122 112 7 1 2 245 363 366
0 5 5 323 305 302 0 6 1 664 647 653	2 0 -2 877 800 880 2 0 3 1203 1230 1212	2 7 -2 503 501 577 2 7 -3 327 336 339	4 0 - 8 598 585 552	5 2 -1 1354 1357 1366	7 1 -4 255 261 256
0 6 2 1002 1102 1112	2 0 -4 613 619 603	2 8 1 153 152 157	4 1 0 651 607 614 4 1 1 215 223 214	5 2 2 374 380 375 5 2 -2 554 542 534	7 1 -8 457 415 410 7 2 1 143 150 148
0 8 1 257 241 243	2 0 7 480 415 438	2 9 -1 58 60 61	4 1 -1 1240 1246 1253	5 2 3 707 700 705	7 2 2 285 287 283
0 8 2 269 292 303 1 1 0 1110 1121 1120	2 0 -8 374 301 300 2 0 -0 261 282 300	3 1 0 383 304 302 3 1 -1 1571 1680 1682	4 1 3 630 608 603	5 2 -4 309 307 310	7 3 0 192 199 187
1 1 1 712 612 599	2 1 0 1877 1999 2015	3 1 2 330 317 302	4 1 -3 586 539 566	5 2 -5 802 803 811 5 3 0 101 112 130	7 3 -1 277 201 270 7 3 -2 473 482 481
1 1 3 195 161 175	2 1 -1 1559 1695 1702	3 1 3 470 425 425	4 1 -7 800 758 760	5 3 -1 274 257 256	7 3 -3 499 495 497
1 1 -3 465 441 429 1 1 4 201 258 257	2 1 2 230 234 230 2 1 -2 455 435 441	3 1 -3 858 841 852 3 1 -4 943 906 911	4 2 0 522 530 519	5 4 0 282 305 299	7 3 -5 364 367 374
1 1 -4 446 440 430	2 1 3 628 590 591	3 1 -5 523 485 486	4 2 1 345 310 300 4 2 -1 1103 1229 1234	5 4 1 014 020 025 5 4 -2 120 112 107	7 4 0 228 275 281
1 1 7 429 423 442	2 1 -6 501 549 546	3 2 0 852 813 825	4 2 4 582 566 569	5 4 -3 962 1005 1018	7 5 1 295 298 304 7 5 -3 182 175 187
1 1 -7 297 323 293 1 1 -8 326 329 328	2 1 -7 038 057 053 2 2 0 483 455 457	3 2 -3 257 233 233 3 2 4 674 659 667	4 2 -5 312 297 283	5 4 -6 229 232 233	8 1 3 101 107 104 8 1 5 264 261 260
1 2 -1 704 656 656	2 2 1 478 421 411	3 2 5 64 53 40 3 2 -5 613 586 568	4 2 -6 241 240 207 4 3 4 174 228 210	5 4 -7 249 237 245 5 4 -8 240 231 235	8 1 -8 597 557 553
1 2 6 402 399 397	2 2 2 188 195 190	3 2 -8 172 208 222	4 3 6 207 236 241	5 5 0 184 187 200 5 5 2 210 226 232	8 3 0 255 275 279 8 3 1 185 213 207
1 2 -0 472 493 493 1 2 7 216 247 240	2 2 -3 874 799 825	3 3 -1 312 288 290	4 3 -7 317 301 286	5 5 -3 194 203 212	9 1 -5 197 189 193
1 2 -7 759 854 881	2 2 4 438 367 380 2 2 - 4 681 624 621	3 3 2 352 317 310 3 3 -2 236 215 218	4 3 -6 270 291 300 4 4 2 191 168 185	5 5 -6 387 379 385	9 3 -2 252 270 267
1 3 -1 379 356 356	2 2 -7 553 633 628	3 3 4 527 498 502	4 4 -2 746 750 732	5 6 0 177 206 207 5 6 -1 57 61 61	9 3 -4 302 305 316 9 4 -2 149 163 164
1 3 2 527 473 491 1 3 -2 194 182 176	2 2 -0 370 479 408 2 3 0 547 532 532	3 3 5 366 365 369	4 4 -3 773 757 742	5 6 -2 332 334 336	9 4 -6 217 221 217
1 3 3 567 532 546	2 3 1 682 644 635	3 3 6 272 275 268	4 4 4 329 344 342	5 ° -3 323 330 337	10 2 -4 310 311 300

ment. A thermal diffuse scattering correction (Cooper & Rouse, 1968) was not applied as this requires a reliable lattice dynamical model. The present study is a necessary step towards this goal. All refinements were based on  $|F_{obs}|$  with unit weights.

The first refinements were carried out by the use of the rigid-body thermal-parameter constraint program (Pawley, 1964). With neutron scattering lengths of 0.66 and 0.65 for carbon and deuterium atoms the conventional R value reached 5.30%, dropping to 5.10% when the scattering lengths for the deuterium positions were reduced to 0.63 to take account of the 2% of hydrogen remaining in the crystal.

Removing the thermal-parameter constraints gave no significant improvement at the 2% level of the *F* dis-

tribution, assuming that  $\left(\frac{R \text{ initial}}{R \text{ final}}\right)^2$  is F distributed

(Pawley, 1966).

We therefore list only the results of the constrained refinement. In Table 1 the calculated structure factors are listed as  $|F_{calc}^{r.b.}|$ . The mean square rigid-body translational and librational tensors are

$$\mathbf{T} = \begin{bmatrix} 4.84 & 0.20 & -0.09 \\ 2.92 & -0.06 \\ 2.29 \end{bmatrix} \dot{A}^2 \times 10^{-2}$$
$$\sigma(\mathbf{T}) = \begin{bmatrix} 0.09 & 0.06 & 0.08 \\ 0.08 & 0.08 & 0.15 \end{bmatrix} \dot{A}^2 \times 10^{-2}$$
$$\mathbf{L} = \begin{bmatrix} 31.59 & -3.49 & 0.11 \\ 18.45 & -1.16 \\ 19.12 \end{bmatrix} \deg^2$$
$$\sigma(\mathbf{L}) = \begin{bmatrix} 1.98 & 0.78 & 1.05 \\ 0.93 & 0.73 \\ 0.85 \end{bmatrix} \deg^2$$

[The use of L instead of the  $\omega$  in the original paper (Cruickshank, 1956) seems now to be generally accepted]. The comparison of these tensors with the cal-

culations on  $C_{10}H_8$  can only be rough, so we must wait for phonon measurements and an improved model before a good comparison can be made.

The nuclear fractional coordinates found in this refinement are listed in Table 2 under the columns headed I symmetry, the molecular site symmetry. The anisotropic temperature factors in this Table are those derived from T and L and the fractional coordinates just mentioned.

The nuclear positions in the coordinate system defined by the inertia axes of the molecule are given in Table 3. The z coordinates are deviations from the plane perpendicular to the axis of greatest inertia. This is the mean molecular plane weighted heavily by the carbon positions. The least-squares standard deviations are 0.0055 and 0.0079 Å for the carbon and deuterium atom positions respectively. The deviations from the mean molecular plane are no more than one standard deviation for the carbon atoms, but about two standard deviations for two of the deuterium atoms. We need to know whether this is evidence for molecular distortion or whether the deviations are insignificant.

To answer this question we should analyse the deviations from *mmm* symmetry, the symmetry of the molecule in the free state. Column 2 of Table 3 shows the x and y coordinates for the symmetry averaged molecule. We see that in three of the eight coordinate pairs averaged, namely  $C_x(A\&E)$ ,  $C_y(A\&E)$  and  $D_x(b\&d)$ , the individuals differ by about three standard deviations. The following analysis shows, however, that these deviations are insignificant.

The most valid test of molecular strain from *mmm* symmetry is given by comparing the results of refinements with and without the symmetry imposed. A new program was written to apply the molecular symmetry constraint throughout the SFLS refinement. The procedure which has been described by Pawley (1969) has been followed. A relatively small number of additions have been made to the usual basic least-squares program with the use of the *Editor* system, written by Dr J.G.Burns of Edinburgh. Unfortunately, the rigid-body thermal parameter constraint program is not

Table 2. Fractional coordinates of the molecule with and without the symmetry constraint,and the thermal parameters for the expressionexp  $[-10^{-4}(h^2b_{11}+k^2b_{22}+l^2b_{33}+2klb_{23}+2lhb_{31}+2hkb_{12})]$  obtained with the rigid body thermal parameter constraint.

	mmm symmetry		T symmetry		Rigid body							
	$\overline{x/a}$	y/b	z/c	$\frac{1}{x/a}$	 y/b	z/c	$\overline{b_{11}}$	b22	b33	b <sub>23</sub>	b <sub>31</sub>	b <sub>12</sub>
C(C)	0.0482	0.1030	0.0359	0.0480	0.1035	0.0352	116	163	174	- 10	69	0
C(B)	0.1149	0.1606	0.2205	0.1155	0.1591	0.2206	202	250	187	-50	87	- 31
C(D)	0.0761	0.2476	-0.0782	0.0755	0.2487	-0.0777	190	200	235	15	118	-18
C(A)	0.0857	0.0174	0.3267	0.0857	0.0164	0.3260	262	357	181	-12	115	3
C(E)	0.0099	0.1869	-0.2555	0.0088	0.1876	-0.2566	251	311	228	52	145	16
D(b)	0.1883	0.3185	0.2733	0.1878	0.3178	0.2718	328	314	253	-119	126	-110
D(d)	0.1499	0.4043	-0.0213	0.1511	0.4053	-0.0219	307	232	338	-6	182	- 89
D(a)	0.1368	0.0627	0.4665	0.1353	0.0630	0.4650	432	561	197	-42	163	- 17
D(e)	0.0318	0.2978	-0.3408	0.0327	0.2972	-0.3414	402	448	311	113	238	14

written in the *Editor* system, so both constraints are not possible simultaneously at present.

The number of parameters needed to determine the nuclear positions for the full-symmetry molecule is 12, compared with 27 in the unconstrained case. Nine of these parameters are indicated in Fig. 1, the remaining three being the three Euler angles necessary to form the rotation matrix which puts the molecule in the correct orientation. This matrix is formed as described by Paw-ley (1969) and the rotated molecule is then transformed to crystal fractional coordinates by the matrix

$$\begin{pmatrix} \frac{1}{a} & 0 & \frac{-\cot}{a}\beta\\ 0 & \frac{1}{b} & 0\\ 0 & 0 & \frac{\csc}{c}\beta \end{pmatrix}.$$

The best starting values for the Euler angles were

$$\varphi = -1.1707^{\circ}$$
$$\theta = -4.3952$$
$$\psi = -2.0597$$

Refinement was carried out by anisotropic temperature factors fixed at the values obtained from the rigid body thermal parameter constraint. The *R* value reached was R=5.15%, with

$$\varphi = -1.1707 \pm 0.0008^{\circ}$$
  

$$\theta = -4.3946 \pm 0.0010$$
  

$$\psi = -2.0592 \pm 0.0012$$

The calculated structure factors are given in Table 1 under the heading  $|F_{calc}^{mmm}|$ .

The atomic coordinates are listed in Tables 2 and 3. This R value is not significantly worse than  $R=5\cdot10\%$ , obtained with the thermal parameter constraint but no symmetry constraint. When the thermal parameters were allowed to vary independently, the R value dropped to R=4.98%. This improvement is not significant on the 25% level of the F distribution, and the results are therefore not given here.

We see in Fig.1 the large difference between the lengths of the bonds C(C)-C(D) and C(D)-C(E). Although this is in agreement with the X-ray result on  $C_{10}H_8$  (Cruickshank, 1957), it is instructive to test the significance of this variation with yet another constrained refinement. Let us take a model for the molecule determined by two parameters, the C-C and the C-D bond lengths. Assume that both rings are perfect hexagons with the C-D bonds pointing radially from the hexagon centres. All the atomic positions in the crystal are now determined by five parameters, the two bond lengths and the three Euler angles.



Fig. 1. The molecule of naphthalene. The capital letters denote the carbon atoms, the small letters the deuterium atoms. The bold arrows indicate the positional parameters consistent with the molecular symmetry. The bond lengths and angles and their errors come from the refinement incorporating the molecular symmetry and using the rigid-body thermal parameters, and are uncorrected for librational motion.

Table 3.	Coordinates	of th	e molec	cule in .	Å

The last columns contain unconstrained coordinates transformed into the inertia axes coordinate system.

Atom	Constrained mmm molecule	Best mmm molecule from next 2 columns	Centrosymmetric molecule, ther- mal parameter constraint	Atom
	-	-	-0.0088	X
C(C)	0.7060	0.7060	0.7076	Y coordinates
	-	<del>-</del> .	-0.0012	Z
	1.2420	1.2399	1.2368 - 1.2429	
C(B)	1.3995	1.3987	1.3982 1.3991	C(D)
	-	· - ·	0.0055 - 0.0055	
	2.4219	2.4220	2.4133 - 2.4307	
C(A)	0.7004	0.6970	0.7046 0.6894	C(E)
	-	_	-0.0008 - 0.0031	
	1.2252	1.2252	1.2043 - 1.2461	
$\mathbf{D}(b)$	2.4781	2.4782	2.4764 2.4800	D(d)
		-	-0.0005 0.0095	
	3.3575	3.3577	3.3453 - 3.3700	
D(a)	1.2359	1.2332	1.2458 1.2205	D(e)
	-	-	-0.0154 0.0155	
С	0.0033	Standard	0.0055	
D	0.0046	deviations	0.0079	

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.

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

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 $(\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoS<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub> 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  $(\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MX<sub>2</sub> 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<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoH<sub>2</sub> (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- $\pi$ -cyclopendadienyl-(toluene-3,4-dithiolato)molybdenum:

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