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The Structure and Electron Density of *sym*-Dibenzo-1,5-cyclooctadiene-3,7-diyne by X-ray Analysis at Three Different Temperatures

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The crystal structure of the title compound (systematic name 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene, $C_{16}H_8$) has been determined at 290, 218 and 113 K. Considerable contraction of cell parameters occurs on cooling, and comparison of bond lengths at the three temperatures provides direct evidence of the apparent bond shortening due to thermal motion. Bond distances agree well after correction according to a rigid-body model. The molecules pack in such a way that the benzene rings are slightly bent out of the plane of the four C_{sp} atoms. The distance between the triple bonds is 2·617 Å at 113 K, and the distortion of the acetylene linkages from the normal linear arrangement is 24·3°. Difference maps reveal an asymmetric distribution of electron density around the triple bonds, with a slight accumulation of charge inside the ring. Experimental findings are confirmed by quantum-mechanical calculations.

Introduction

Correction of intramolecular interatomic distances foreshortened by rigid-body motion is today a routine procedure in crystallographic studies. However, owing to the lack of an absolute criterion to gauge the adequacy of the rigid-body approximation for the molecule under study, no warranty exists that the corrections do not suffer from systematic errors.

To estimate the reliability of these corrections, applied on the basis of the **TLS** analysis (Schomaker & Trueblood, 1968) to the room-temperature data of *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (SDCD), we have determined the structure at two lower temperatures, 218 and 113 K. The agreement between the corrected values of the bond lengths at 290 and 218 K and those found at 113 K (only slightly affected by thermal motion) can be assumed to be a measure of the reliability of the proposed rigid-body model. It should be pointed out that usual evaluations indicate that SDCD behaves as a rigid body only to a first approximation, since the room-temperature data analysis gives the root mean square residue $\Delta U_{\rm RMS} = \langle (U_{\rm obs} - U_{\rm calc})^2 \rangle^{1/2}$ a value equal to $2\sigma_{\rm RMS}(U_{\rm obs})$. The results of the present study show that even under such circumstances the thermal corrections can be safely applied.

Low-temperature data were collected also to elucidate, at least in a qualitative way, the electron-density distribution at the bonds between atoms of the highly strained central ring of the molecule. An account of the molecular geometry at room temperature has been given (Destro, Pilati & Simonetta, 1975).

Experimental

A sample of the substance, kindly supplied by Professor F. Sondheimer, was recrystallized from tetrahydrofuran by slow evaporation at −10°C; a unique, yellow, prismatic crystal, with cross-section about 0·32 × 0·30 mm and height about 0·75 mm, was obtained. It was cut to yield two specimens of approximately equal volume. The first produced the data set at room temperature (290 K); after several hours of exposure to air and X-rays it showed a gradual darkening, indicating noticeable decomposition at this temperature. Hence the second crystal was used for the data collection at 218 and 113 K, and for the determination of cell parameters at five different temperatures in the range 113–290 K. No decomposition was detected in the second crystal below 250 K.

Both samples were glued on the top of Lindemann glass capillaries. After the data collection at 218 K, a too fast cooling to a lower temperature cracked the crystal in the region of the glue. The larger portion was recovered and mounted on a new glass fibre; the volume of the lost slice was less than a tenth of the total volume.

Data were collected on a computer-controlled Syntex $P\bar{1}$ diffractometer equipped with the low-temperature LT-1 device (Syntex Analytical Instruments). The temperatures were measured by placing the junction of an accurately calibrated thermocouple in the same position as the crystal. The temperature variation in reproducing the same cooling conditions was less than 1 K, and variations in the gas stream did not exceed 2 K within a cubic volume of 2 mm side. An inclusive error of ±5 K may be safely associated with each temperature measurement.

The graphite-monochromated radiations used for intensity measurements were Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) at room temperature ($2\theta_{\max} = 140°$) and Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) at 218 and 113 K ($2\theta_{\max} = 54{\cdot}9°$). A variable rate θ–2θ scan technique was employed; background was monitored for a time equal to one-half the scan time at each extremum. Check reflexions indicated a general downward trend in the intensity at 290 K, whereas no appreciable drift was noticed at the lower temperatures. Observational variances $\sigma^2(I)$ included counting statistics plus an additional term, $(0{\cdot}03S)^2$, where S is the scan count. Intensities and their e.s.d.'s were corrected for Lorentz and polarization effects, but not for absorption; to those collected at room temperature a decay correction linearly dependent on time was applied.

Cell dimensions

After the collection of the three sets of intensities, 30 reflexions with $36 < 2\theta < 46°$ were accurately centred at five different temperatures. From the least-squares fit to their $\sin^2\theta$ measurements, cell parameters at each temperature were obtained; the values at 290, 218 and 113 K are listed in Table 1, with other crystal data. The dependence of the cell parameters on the absolute temperature T may be expressed by:

$$a = a_0(0{\cdot}9757 + 41{\cdot}46 \times 10^{-6}T + 0{\cdot}1462 \times 10^{-6}T^2);$$

$$b = b_0(0{\cdot}9952 + 16{\cdot}74 \times 10^{-6}T);$$

$$c = c_0(0{\cdot}9883 + 23{\cdot}53 \times 10^{-6}T + 0{\cdot}0580 \times 10^{-6}T^2);$$

$$\beta = \beta_0(1{\cdot}0109 - 26{\cdot}30 \times 10^{-6}T - 0{\cdot}0398 \times 10^{-6}T^2);$$

$$V = V_0(0{\cdot}9588 + 85{\cdot}43 \times 10^{-6}T + 0{\cdot}1956 \times 10^{-6}T^2),$$

where the subscript 0 refers to 290 K. These equations were obtained by a least-squares treatment of the five sets of parameters, and are represented in Fig. 1. Linear and volumetric expansion coefficients may be derived from the equations; their average values in the range 113–290 K, multiplied by 10^6, are $\alpha_a = 101$, $\alpha_b = 17$, $\alpha_c = 47$, and $\alpha_V = 167$ K^{-1}.

Table 1. *Crystal data*

$C_{16}H_8$ F.W. 200·24
Space group $P2_1/n$ $Z = 4$
μ(Cu $K\alpha$) = 5·75 cm^{-1} μ(Mo $K\alpha$) = 0·80 cm^{-1}

	290 K	218 K	113 K
a	6·1479 (7) Å	6·0970 (8) Å	6·0388 (12) Å
b	11·8392 (9)	11·8282 (11)	11·8041 (18)
c	14·0334 (13)	13·9786 (14)	13·9163 (24)
β	91·02 (1)°	91·32 (1)°	91·69 (2)°
V	1021·3 (2) Å^3	1007·8 (3) Å^3	991·6 (7) Å^3
d_x (g cm^{-3})	1·302	1·320	1·341

Refinement

The function minimized in the refinement of the three sets of data was $\Sigma\, w(|F_o| - k|F_c|)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$. In the final cycles, 178 parameters were included in a single matrix and adjusted: coordinates and anisotropic temperature parameters for the 16 C atoms, coordinates and isotropic temperature factors for the eight H atoms, a scale factor and a secondary extinction parameter [Larson (1967), equation (3)]. Atomic form factors for C were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). Final values for the parameters of the C atoms are given in Table 2, and of the H atoms in Table 3. Observed and calculated structure factors are given in Table 4.* Final agreement indices are listed in Table 5. The numbering scheme is shown in Fig. 2.

Analysis of the thermal motion

The anisotropic thermal parameters for all 16 C atoms were used to determine the rigid-body motion of the SDCD molecule (Schomaker & Trueblood, 1968). The results are given in Table 6. At each temperature the

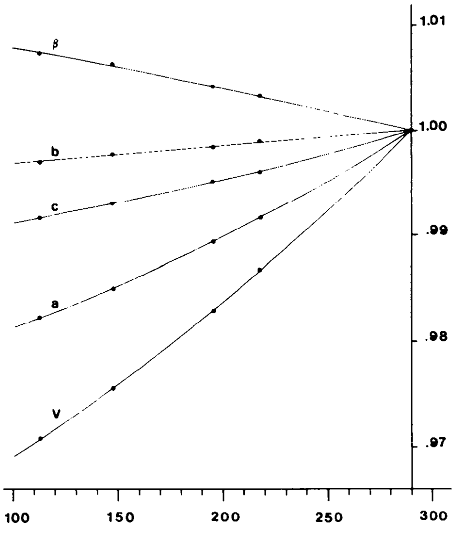

Fig. 1. Variation of cell parameters with temperature (K). For each parameter, the value at 290 K is set equal to unity.

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* Table 4 (structure factors) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32057 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

root mean square residue ΔU_{RMS} is approximately equal to $2\sigma_{\mathrm{RMS}}(U_{\mathrm{obs}})$: this seems to indicate that the molecule behaves as a rigid body only to a first approximation. However, in view of the substantial agreement between the corrected values of the bond lengths at room temperature and the corresponding ones found at 113 K (see next section), the rigid-body model seems in this instance a fairly good approximation. Hence, a more adequate estimate of the fit is perhaps the average disagreement index

Table 2. *Final coordinates and thermal parameters for the carbon atoms*

Fractional coordinates are $\times 10^5$, thermal parameters $\times 10^4$. The anisotropic temperature coefficients are of the form: $T_i = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
290 K									
C(1)	40943 (31)	33953 (14)	58381 (11)	391 (6)	77 (1)	54 (1)	13 (2)	−6 (2)	−8 (1)
C(2)	56709 (33)	41892 (14)	60912 (12)	511 (7)	69 (1)	59 (1)	7 (2)	−27 (2)	−16 (1)
C(3)	76446 (32)	41896 (13)	56546 (12)	458 (7)	66 (1)	62 (1)	−31 (2)	−31 (2)	−4 (1)
C(4)	81197 (29)	33982 (12)	49572 (11)	376 (5)	65 (1)	59 (1)	−33 (2)	−14 (2)	1 (1)
C(5)	68469 (23)	17160 (12)	39963 (10)	269 (4)	65 (1)	49 (1)	−16 (2)	2 (1)	2 (1)
C(6)	63295 (22)	9025 (12)	35372 (9)	258 (4)	68 (1)	47 (1)	−6 (2)	7 (1)	1 (1)
C(7)	53726 (26)	−8510 (12)	25881 (10)	338 (5)	72 (1)	49 (1)	−2 (2)	−3 (2)	−6 (1)
C(8)	38411 (28)	−16787 (13)	23764 (10)	414 (6)	65 (1)	49 (1)	−6 (2)	−17 (2)	−8 (1)
C(9)	18509 (28)	−16755 (13)	28079 (11)	387 (6)	66 (1)	55 (1)	−36 (2)	−33 (2)	2 (1)
C(10)	13444 (26)	−8457 (13)	34671 (10)	311 (5)	75 (1)	50 (1)	−31 (2)	−13 (1)	5 (1)
C(11)	25623 (21)	8934 (12)	43687 (9)	257 (4)	72 (1)	46 (1)	−2 (2)	0 (1)	1 (1)
C(12)	30761 (23)	17089 (12)	48254 (9)	272 (4)	72 (1)	46 (1)	2 (2)	4 (1)	−1 (1)
C(13)	45202 (23)	25962 (11)	51440 (9)	319 (4)	61 (1)	44 (1)	7 (2)	−14 (1)	0 (1)
C(14)	65757 (23)	25986 (11)	46921 (9)	311 (4)	55 (1)	46 (1)	−6 (2)	−14 (1)	4 (1)
C(15)	49067 (23)	−48 (11)	32380 (9)	287 (4)	58 (1)	40 (1)	−4 (2)	−10 (1)	3 (1)
C(16)	28404 (22)	−74 (11)	36912 (9)	276 (4)	60 (1)	40 (1)	−6 (2)	−10 (1)	3 (1)
218 K									
C(1)	41157 (26)	33973 (12)	58386 (10)	247 (4)	53 (1)	39 (1)	12 (2)	−2 (1)	−5 (1)
C(2)	57042 (27)	41945 (13)	60898 (11)	340 (5)	47 (1)	39 (1)	7 (2)	−13 (2)	−10 (1)
C(3)	76998 (27)	41976 (12)	56532 (10)	307 (5)	43 (1)	44 (1)	−25 (2)	−23 (2)	−1 (1)
C(4)	81686 (24)	33996 (12)	49545 (10)	238 (4)	45 (1)	39 (1)	−21 (2)	−8 (1)	2 (1)
C(5)	68827 (20)	17062 (11)	39936 (9)	154 (3)	47 (1)	34 (1)	−11 (2)	4 (1)	3 (1)
C(6)	63561 (20)	8905 (11)	35344 (9)	161 (3)	48 (1)	31 (1)	−1 (2)	8 (1)	1 (1)
C(7)	53808 (23)	−8670 (12)	25811 (9)	206 (4)	51 (1)	33 (1)	3 (2)	1 (1)	−3 (1)
C(8)	38285 (24)	−17009 (12)	23698 (9)	277 (5)	45 (1)	34 (1)	0 (2)	−10 (1)	−6 (1)
C(9)	18262 (24)	−16957 (12)	28047 (10)	252 (4)	43 (1)	38 (1)	−27 (2)	−23 (1)	2 (1)
C(10)	13248 (23)	−8625 (12)	34683 (10)	193 (4)	51 (1)	35 (1)	−18 (2)	−8 (1)	4 (1)
C(11)	25667 (20)	8802 (12)	43671 (9)	153 (3)	51 (1)	32 (1)	−2 (2)	3 (1)	3 (1)
C(12)	30861 (21)	17006 (12)	48266 (9)	169 (3)	51 (1)	32 (1)	5 (2)	5 (1)	1 (1)
C(13)	45393 (21)	25956 (11)	51439 (8)	201 (4)	41 (1)	31 (1)	2 (2)	−10 (1)	1 (1)
C(14)	66165 (21)	25962 (11)	46900 (8)	202 (4)	37 (1)	31 (1)	−1 (2)	−9 (1)	2 (1)
C(15)	49190 (21)	−197 (11)	32331 (9)	181 (4)	40 (1)	28 (1)	−2 (1)	−7 (1)	3 (1)
C(16)	28412 (20)	−211 (11)	36908 (8)	180 (4)	40 (1)	27 (1)	−3 (1)	−7 (1)	3 (1)
113 K									
C(1)	41438 (21)	33995 (10)	58393 (8)	132 (3)	30 (1)	20 (1)	7 (1)	0 (1)	−1 (1)
C(2)	57532 (21)	42024 (10)	60888 (9)	185 (4)	24 (1)	20 (1)	5 (1)	−7 (1)	−5 (1)
C(3)	77724 (21)	41992 (10)	56500 (8)	166 (4)	23 (1)	23 (1)	−14 (1)	−12 (1)	0 (1)
C(4)	82393 (20)	33957 (10)	49494 (8)	130 (4)	25 (1)	20 (1)	−8 (1)	−4 (1)	2 (1)
C(5)	69250 (18)	16962 (9)	39896 (8)	85 (3)	26 (1)	19 (1)	−5 (1)	2 (1)	3 (1)
C(6)	63836 (18)	8737 (9)	35272 (8)	89 (3)	27 (1)	17 (1)	2 (1)	5 (1)	3 (1)
C(7)	53847 (19)	−8853 (10)	25717 (8)	114 (3)	28 (1)	17 (1)	3 (1)	0 (1)	0 (1)
C(8)	38145 (20)	−17232 (10)	23605 (8)	153 (3)	24 (1)	18 (1)	2 (1)	−8 (1)	−2 (1)
C(9)	17889 (20)	−17185 (10)	28022 (8)	133 (3)	24 (1)	21 (1)	−15 (1)	−14 (1)	3 (1)
C(10)	12947 (19)	−8824 (10)	34704 (8)	108 (3)	28 (1)	17 (1)	−8 (1)	−5 (1)	3 (1)
C(11)	25694 (17)	8669 (10)	43702 (7)	84 (3)	29 (1)	17 (1)	0 (1)	4 (1)	3 (1)
C(12)	30988 (18)	16920 (10)	48283 (7)	93 (3)	29 (1)	17 (1)	4 (1)	4 (1)	1 (1)
C(13)	45698 (18)	25903 (9)	51423 (7)	118 (3)	22 (1)	17 (1)	0 (1)	−8 (1)	2 (1)
C(14)	66626 (18)	25899 (9)	46868 (7)	115 (3)	21 (1)	16 (1)	2 (1)	−6 (1)	2 (1)
C(15)	49272 (18)	−381 (9)	32282 (8)	103 (3)	22 (1)	16 (1)	−2 (1)	−5 (1)	2 (1)
C(16)	28381 (18)	−394 (9)	36895 (7)	103 (3)	21 (1)	15 (1)	0 (1)	−3 (1)	2 (1)

$\langle |U_{\text{obs}} - U_{\text{calc}}|/|U_{\text{obs}}| \rangle$, and values less than 10% for this quantity can be assumed as indicative of a satisfactory fit.

The librational motion is strongly anisotropic: as expected, the principal axis of libration is nearly along the axis of minimum inertia (axis N in Fig. 2). The moment of inertia around this axis is eight times smaller than that around the maximum inertial axis L; the inertia about the third axis (M) is very similar in magnitude to that about L, being < 15% smaller. The translational motion exhibits only a slight anisotropy at each temperature; the minimum molecular translation occurs in a direction nearly parallel to **b**, *i.e.* the axis which undergoes the minimum variation with the temperature (Fig. 1).

As the temperature goes down from 290 to 113 K, the root mean square amplitudes of the translational and librational displacements decrease to about one-third of the original.

Table 3. *Coordinates* ($\times 10^4$) *and isotropic temperature coefficients* ($\times 10$) *for the hydrogen atoms*

	x	y	z	B
290 K				
H(1)	2718 (29)	3365 (14)	6144 (12)	65 (4)
H(2)	5351 (27)	4742 (15)	6557 (12)	67 (4)
H(3)	8807 (28)	4771 (14)	5855 (12)	70 (4)
H(4)	9624 (28)	3413 (14)	4654 (11)	67 (4)
H(7)	6853 (27)	−831 (13)	2247 (11)	63 (4)
H(8)	4191 (26)	−2296 (13)	1924 (11)	59 (4)
H(9)	792 (27)	−2273 (13)	2666 (10)	60 (4)
H(10)	−77 (25)	−840 (13)	3795 (10)	57 (4)
218 K				
H(1)	2713 (24)	3379 (12)	6167 (9)	42 (3)
H(2)	5389 (24)	4715 (12)	6565 (10)	43 (3)
H(3)	8815 (26)	4762 (13)	5848 (11)	50 (4)
H(4)	9615 (24)	3410 (12)	4635 (9)	43 (3)
H(7)	6822 (24)	−870 (12)	2271 (10)	41 (3)
H(8)	4169 (22)	−2298 (12)	1922 (10)	38 (3)
H(9)	770 (24)	−2269 (12)	2653 (9)	42 (3)
H(10)	−88 (25)	−843 (12)	3812 (10)	44 (3)
113 K				
H(1)	2728 (23)	3381 (11)	6157 (9)	26 (3)
H(2)	5440 (23)	4743 (12)	6570 (10)	30 (3)
H(3)	8901 (26)	4769 (13)	5821 (10)	36 (3)
H(4)	9722 (23)	3388 (11)	4643 (9)	26 (3)
H(7)	6842 (23)	−885 (11)	2260 (9)	25 (3)
H(8)	4150 (22)	−2330 (11)	1911 (9)	24 (3)
H(9)	696 (24)	−2304 (12)	2657 (9)	29 (3)
H(10)	−141 (22)	−862 (11)	3805 (9)	23 (3)

Table 5. *Agreement indices of least-squares refinement*

	290 K	218 K	113 K
k (scale factor)	18·281 (7)	6·221 (2)	6·730 (2)
g (isotropic extinction coefficient) $\times 10^7$	346 (31)	72 (15)	62 (17)
N_T (total number of independent reflexions measured)	1910	2307	2276
N_o (number of reflexions judged as observed, having $F_o > 0$, and included in the refinement)	1775	2093	2138
N [number of reflexions with $F_o^2 > 3\sigma(F_o^2)$]	1459	1547	1696
V (number of variables)	178	178	178
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(N_o - V)]^{1/2}$	1·99	1·70	1·63
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ $R(N_o)$	0·045	0·053	0·046
$R(N)$	0·035	0·037	0·035
$R_w(N_o) = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w(F_o)^2]^{1/2}$	0·053	0·045	0·046

Molecular structure

The bond distances and angles of SDCD are listed in Tables 7 and 8 respectively. The correction for apparent bond shortening due to thermal motion is very small at 113 K, but appreciable at the other two temperatures. As expected from the results of the rigid-body **TLS** analysis, the correction is largest for the bonds perpendicular to the axis of minimum inertia, whereas the change in the triple-bond lengths is only marginally significant.

The comparison of the three sets of corrected values (Table 7) shows that the agreement is satisfactory: even if some of the bond lengths at 290 K appear either undercorrected or systematically shortened, no difference between two corresponding values at 290 and 113 K is greater than three times the individual e.s.d. The greatest difference between corresponding values at 218 and 113 K is also $< 3\sigma$.

The precision of the three structure determinations is shown by the agreement of the bond angles (Table 8). Even for angles involving H atoms, the difference between each individual value and the average rarely exceeds the estimated standard deviation.

The molecular strain, especially at the central eight-membered ring, is clearly evidenced by the deviation of bond distances and angles from their normal values. Of particular relevance are (i) the lengthening of the $C_{sp^2}—C_{sp^2}$ inner bonds C(13)—C(14) and C(15)—C(16) (1·431 Å at 113 K before thermal correction), and (ii)

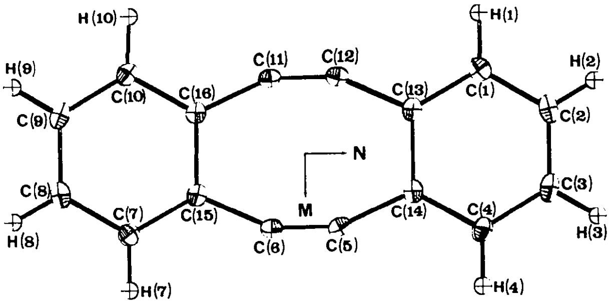


Fig. 2. 40% probability thermal ellipsoids at 113 K (Johnson, 1965). The molecule is viewed along L, the direction corresponding to the maximum moment of inertia.

Table 6. *Rigid-body-motion parameters*

The tensors are referred to a Cartesian coordinate system defined by unit vectors $\hat{\mathbf{a}}^*$, $\hat{\mathbf{b}}$, $\hat{\mathbf{a}}^* \times \hat{\mathbf{b}}$. Standard deviations are given in parentheses.

290 K

$[\Sigma(U_{\rm obs}-U_{\rm calc})^2/(m-s)]^{1/2}$	0·0017	$\Delta U_{\rm RMS}=\langle(U_{\rm obs}-U_{\rm calc})^2\rangle^{1/2}$	0·0015
$\langle\lvert U_{\rm obs}-U_{\rm calc}\rvert/\lvert U_{\rm obs}\rvert\rangle$	3·7%	$\sigma_{\rm RMS}(U_{\rm obs})$	0·0008

T (Å² × 10⁴) ('unreduced')			**L** (rad² × 10⁴)			**S** (Å rad × 10⁴) [trace (S) = 0]		
1861 (137)	−122 (27)	−646 (68)	17 (1)	14 (2)	15 (1)	−59 (10)	57 (5)	18 (4)
	809 (35)	46 (17)		49 (5)	23 (4)	−258 (27)	18 (6)	114 (13)
		652 (27)			38 (3)	−88 (17)	−27 (5)	41 (9)

Principal axes	Eigenvalues	Direction cosines† (× 10⁴)			Direction cosines relative to inertial axes L, M, N (× 10⁴)		
	24·2	3299	7329	5950	1119	341	9931
L [(°)²]	6·9	2418	−6748	6972	9896	−944	−1082
	3·1	9125	−862	−3999	901	9950	−443
	0·0494	−508	1131	9923	6296	−4852	6068
Reduced **T** (Å²)	0·0423	9960	−676	587	4394	8665	2370
	0·0330	738	9913	−1092	−6407	1175	7588

218 K

$[\Sigma(U_{\rm obs}-U_{\rm calc})^2/(m-s)]^{1/2}$	0·0017	$\Delta U_{\rm RMS}=\langle(U_{\rm obs}-U_{\rm calc})^2\rangle^{1/2}$	0·0015
$\langle\lvert U_{\rm obs}-U_{\rm calc}\rvert/\lvert U_{\rm obs}\rvert\rangle$	5·5%	$\sigma_{\rm RMS}(U_{\rm obs})$	0·0007

T (Å² × 10⁴) ('unreduced')			**L** (rad² × 10⁴)			**S** (Å rad × 10⁴) [trace (S) = 0]		
1220 (134)	−93 (31)	−428 (66)	12 (1)	10 (2)	11 (1)	−41 (10)	38 (5)	13 (4)
	542 (34)	47 (16)		33 (5)	15 (4)	−175 (27)	15 (5)	77 (13)
		444 (26)			27 (3)	−56 (17)	−16 (5)	26 (8)

Principal axes	Eigenvalues	Direction cosines† (× 10⁴)			Direction cosines relative to inertial axes L, M, N (× 10⁴)		
	16·6	3425	7210	6024	1319	421	9904
L [(°)²]	5·0	2246	−6854	6927	9861	−1077	−1268
	2·0	9123	−1020	−3967	1014	9933	−557
	0·0307	7194	−888	−6889	−1867	9500	−2503
Reduced **T** (Å²)	0·0283	−6902	204	−7234	−7824	−2979	−5470
	0·0222	782	9958	−466	−5942	936	7988

113 K

$[\Sigma(U_{\rm obs}-U_{\rm calc})^2/(m-s)]^{1/2}$	0·0013	$\Delta U_{\rm RMS}=\langle(U_{\rm obs}-U_{\rm calc})^2\rangle^{1/2}$	0·0011
$\langle\lvert U_{\rm obs}-U_{\rm calc}\rvert/\lvert U_{\rm obs}\rvert\rangle$	8·0%	$\sigma_{\rm RMS}(U_{\rm obs})$	0·0005

T (Å² × 10⁴) ('unreduced')			**L** (rad² × 10⁴)			**S** (Å rad × 10⁴) [trace (S) = 0]		
575 (100)	−40 (23)	−187 (48)	5 (1)	4 (1)	5 (1)	−17 (7)	16 (4)	5 (3)
	267 (25)	34 (12)		15 (4)	6 (3)	−78 (20)	8 (4)	33 (9)
		218 (18)			13 (2)	−22 (13)	−6 (4)	9 (6)

Principal axes	Eigenvalues	Direction cosines† (× 10⁴)			Direction cosines relative to inertial axes L, M, N (× 10⁴)		
	7·5	3624	6927	6236	1737	496	9836
L [(°)²]	2·5	2149	−7131	6673	9802	−1052	−1678
	0·8	9069	−1078	−4073	952	9932	−669
	0·0174	8148	−1461	−5610	−266	9788	−2030
Reduced **T** (Å²)	0·0159	−5620	385	−8263	−8229	−1367	−5516
	0·0119	1423	9885	−508	−5677	1524	8090

† Referred to the Cartesian coordinate system used for the tensors.

the deviation, 24·3°, of the acetylene linkages from linearity. The same trend is present in 1,5-cyclooctadiyne for which some structural details, obtained by Rømming by X-ray diffraction at −170 °C, are reported by Kloster-Jensen & Wirz (1975). In the latter compound the contact between the triple bonds (2·597 *vs* 2·617 Å in SDCD) is mainly relieved by a lengthening of the two C_{sp^3}—C_{sp^3} bonds (1·570 Å), and consequently the deformation of the angles at the C_{sp} atoms is less pronounced than in our molecule (20·7 *vs* 24·3°).

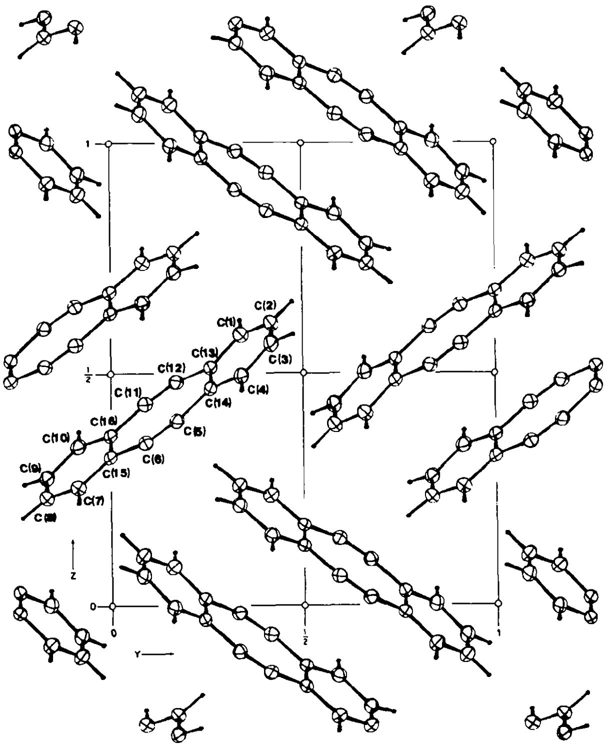


Fig. 3. A drawing of the structure viewed down **a**.

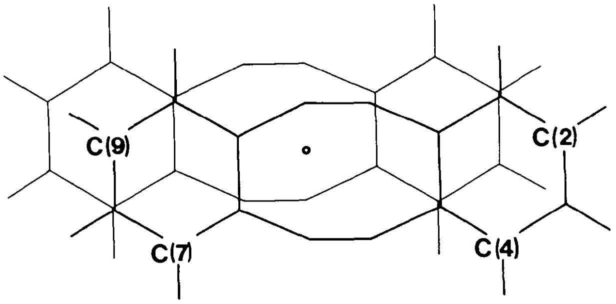


Fig. 4. A drawing of two molecules related by a centre of symmetry, viewed perpendicular to their planes.

Table 7. *Bond lengths* (Å)

	290 K		218 K		113 K	
	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
(*a*) C–C						
C(1)–C(2)	1·392	1·395	1·391	1·393	1·394	1·396
C(2)–C(3)	1·369	1·376	1·374	1·378	1·380	1·382
C(3)–C(4)	1·390	1·393	1·393	1·395	1·396	1·397
C(4)–C(14)	1·387	1·390	1·385	1·387	1·388	1·389
C(14)–C(5)	1·442	1·445	1·446	1·448	1·446	1·447
C(5)–C(6)	1·199	1·200	1·199	1·200	1·205	1·206
C(6)–C(15)	1·443	1·446	1·445	1·447	1·444	1·445
C(15)–C(7)	1·388	1·392	1·388	1·390	1·389	1·390
C(7)–C(8)	1·388	1·391	1·394	1·396	1·396	1·397
C(8)–C(9)	1·375	1·381	1·376	1·381	1·385	1·387
C(9)–C(10)	1·389	1·392	1·392	1·395	1·395	1·396
C(10)–C(16)	1·386	1·389	1·389	1·391	1·392	1·393
C(16)–C(11)	1·441	1·444	1·437	1·440	1·442	1·443
C(11)–C(12)	1·198	1·200	1·202	1·204	1·203	1·203
C(12)–C(13)	1·441	1·444	1·444	1·446	1·443	1·444
C(13)–C(1)	1·386	1·390	1·386	1·388	1·391	1·393
C(13)–C(14)	1·424	1·431	1·430	1·434	1·430	1·433
C(15)–C(16)	1·431	1·438	1·432	1·437	1·432	1·434
σ(C–C)	0·0019–0·0027		0·0017–0·0023		0·0015–0·0018	
(*b*) C–H						
C(1)–H(1)	0·96		0·98		0·97	
C(2)–H(2)	0·95		0·93		0·95	
C(3)–H(3)	1·03		0·99		0·98	
C(4)–H(4)	1·02		1·00		1·00	
C(7)–H(7)	1·04		0·99		0·99	
C(8)–H(8)	0·99		0·97		0·98	
C(9)–H(9)	0·98		0·96		0·97	
C(10)–H(10)	0·99		1·00		1·00	
σ(C–H)	0·016–0·018		0·014–0·016		0·013–0·015	

A feature of SDCD is the slight but significant non-planarity of the molecules in the crystal (Table 9). The small deformation of the system from strict planarity occurs in such a way that benzene rings of molecules related by centres of symmetry (Fig. 3) attract each other, and consequently each molecule assumes a scarcely perceptible 'butterfly' shape. As shown in Fig. 4, the maximum overlap is between C(1) and C(8) (at $1-x, -y, 1-z$); their separation is 3·451, 3·424 and 3·397 Å at 290, 218 and 113 K respectively. The other closest contacts are C(10)···C(14), 3·462, and C(12)···C(15), 3·517 Å (values at 113 K). The distance between the planes passing through the C_{sp} atoms of the two centrosymmetrically related molecules is 3·522 Å at 113 K.

Table 8. *Bond angles* (°)

	290 K	218 K	113 K	Average
(*a*) $C-\hat{C}-C$				
C(13)–C(1)–C(2)	120·1	120·1	119·9	120·0
C(1)–C(2)–C(3)	120·3	120·5	120·4	120·4
C(2)–C(3)–C(4)	120·9	120·5	120·7	120·7
C(3)–C(4)–C(14)	119·9	120·1	120·0	120·0
C(14)–C(5)–C(6)	156·0	156·1	156·0	156·0
C(5)–C(6)–C(15)	155·3	155·4	155·3	155·3
C(15)–C(7)–C(8)	120·2	120·2	120·2	120·2
C(7)–C(8)–C(9)	120·6	120·5	120·5	120·5
C(8)–C(9)–C(10)	120·5	120·5	120·5	120·5
C(9)–C(10)–C(16)	120·1	120·1	119·9	120·0
C(16)–C(11)–C(12)	156·4	156·5	156·5	156·5
C(11)–C(12)–C(13)	155·3	155·3	155·2	155·3
C(12)–C(13)–C(14)	114·2	114·1	114·2	114·2
C(12)–C(13)–C(1)	126·3	126·4	126·3	126·3
C(1)–C(13)–C(14)	119·5	119·5	119·6	119·5
C(13)–C(14)–C(5)	114·5	114·4	114·4	114·4
C(4)–C(14)–C(5)	126·1	126·3	126·1	126·2
C(4)–C(14)–C(13)	119·4	119·2	119·4	119·3
C(6)–C(15)–C(16)	114·2	114·0	114·1	114·1
C(6)–C(15)–C(7)	126·7	126·8	126·6	126·7
C(7)–C(15)–C(16)	119·1	119·2	119·3	119·2
C(15)–C(16)–C(11)	114·1	114·2	114·3	114·2
C(11)–C(16)–C(10)	126·4	126·3	126·0	126·2
C(10)–C(16)–C(15)	119·4	119·5	119·7	119·5
Range of e.s.d.'s ($\times 10^2$)	11–16	11–14	9–12	
(*b*) $C-\hat{C}-H$				
C(13)–C(1)–H(1)	118·0	119·5	119·0	118·8
C(2)–C(1)–H(1)	121·9	120·4	121·1	121·1
C(1)–C(2)–H(2)	119·3	118·4	118·8	118·8
C(3)–C(2)–H(2)	120·3	121·0	120·8	120·7
C(2)–C(3)–H(3)	119·7	119·4	120·4	119·8
C(4)–C(3)–H(3)	119·4	120·0	118·9	119·4
C(3)–C(4)–H(4)	118·9	120·2	120·3	119·8
C(14)–C(4)–H(4)	121·2	119·6	119·7	120·2
C(15)–C(7)–H(7)	118·7	119·1	118·9	118·9
C(8)–C(7)–H(7)	121·1	120·7	120·9	120·9
C(7)–C(8)–H(8)	120·1	119·8	120·2	120·0
C(9)–C(8)–H(8)	119·2	119·6	119·3	119·4
C(8)–C(9)–H(9)	120·1	120·0	120·4	120·2
C(10)–C(9)–H(9)	119·4	119·5	119·0	119·3
C(9)–C(10)–H(10)	121·4	122·9	122·4	122·2
C(16)–C(10)–H(10)	118·4	117·0	117·8	117·7
Range of e.s.d.'s ($\times 10$)	9–10	8–9	7–9	

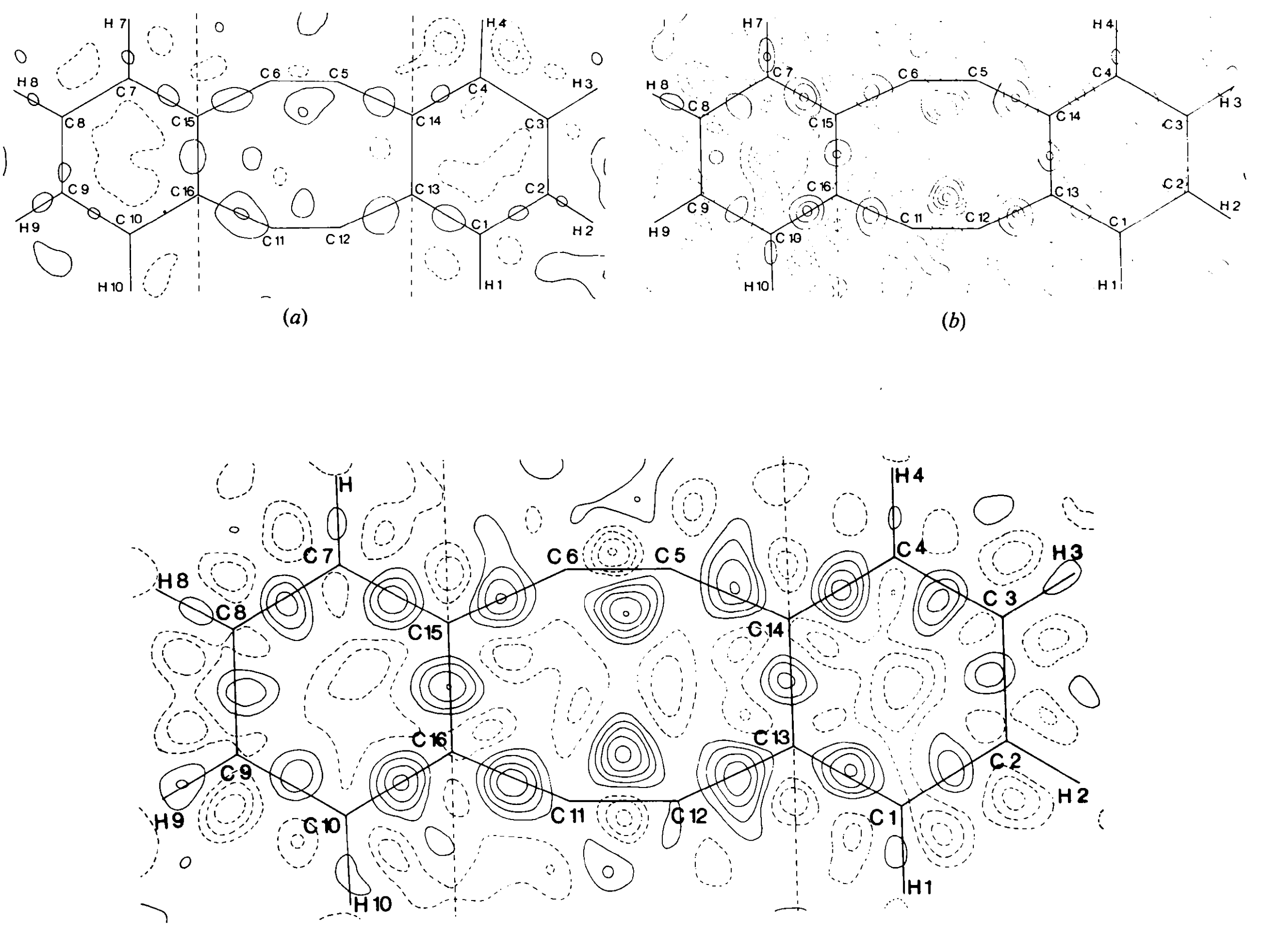
Electron density

Difference syntheses, calculated in the planes of the benzene rings and in the plane passing through the four C_{sp} atoms, are shown in Fig. 5; only reflexions with $|F_c| \geq \frac{1}{2}F_o$ were included in the calculations. The errors in the electron-density residues, derived from estimated σ's of the observed data (Cruickshank, 1949), are 0·02, 0·05 and 0·04 e Å^{-3} at 290, 218 and 113 K respectively. Although the peaks, as expected, are much less pronounced at room temperature, the same essential features are present in all three maps.

As with the results of previous studies of benzene derivatives (O'Connell, Rae & Maslen, 1966, and references therein), the difference densities in the regions of the benzene rings of SDCD are characterized by deep troughs in the centre of the rings, negative regions antisymmetric to the bonds, and excess of density between bonded atoms.

The most interesting feature of the maps concerns the central eight-membered ring, and particularly the region close to the triple bonds. At 113 K, two positive peaks of 0·26 e Å^{-3} show up in the ring plane; they are located at 0·5 Å from the centre of the bonds, in a direction perpendicular to them and pointing towards the centre of the ring. As a counterpart, two negative residues appear outside the ring, with their minima (–0·18 e Å^{-3}) 0·2 Å from the C≡C bonds. The 113 K difference density section perpendicular to the bonds at their centres is shown in Fig. 6. A trough of –0·2 e Å^{-3} in the centre of the triple bond as well as a peak of 0·1 e Å^{-3} at 0·6 Å from the centre of the bond were found by Irngartinger, Leiserowitz & Schmidt (1970) in the room-temperature averaged electron density distribution of a molecule which consists of three identical $-C_6H_4-C\equiv C-$ subunits, 1:2,5:6,9:10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne. In this compound the triple bonds do not show any significant distortion, the average value of the six C–C≡C angles being 178·3°. According to the authors, the above-mentioned effects are due to 'errors inherent in the determination of atomic thermal parameters from room-temperature X-ray data up to the usual sin θ/λ limit of 0·66 Å^{-1}'. Since the deep negative residue is found also in our low-temperature difference density, it can be more generally stated that the main reason for the artefact is the spherical-atom scattering factor formalism, as confirmed by the theoretical study of Ruysink & Vos (1974*a*) on an ethyne model structure.

On the other hand, the positive residues at 0·5 Å from the triple bonds of SDCD are certainly not an artefact, as we have confirmed by an *ab initio* SCF



(*a*) (*b*)

(*c*)

Fig. 5. Sections of the ΔF syntheses showing residual electron density. The three sections of each composite, separated by chain-dotted lines, are defined by the planes through the benzene rings and the plane through the triple bonds. Contour levels at intervals of 0·05 e Å^{-3}; solid lines positive; dashed lines negative; zero contours omitted. (*a*) 290 K; (*b*) 218 K; (*c*) 113 K.

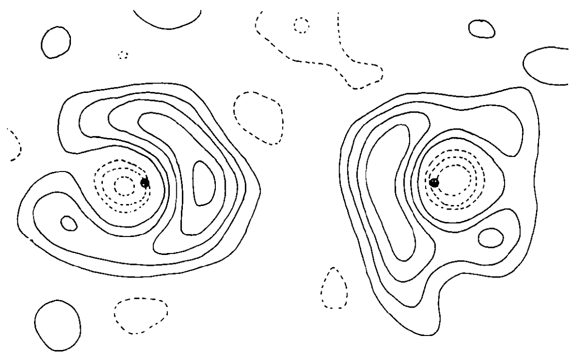


Fig. 6. Difference density section perpendicular to the triple bonds at their centres at 113 K. Contours as in Fig. 5. The centre of the C(11)—C(12) bond is represented by the shaded circle on the left, that of the C(5)—C(6) bond by the shaded circle on the right.

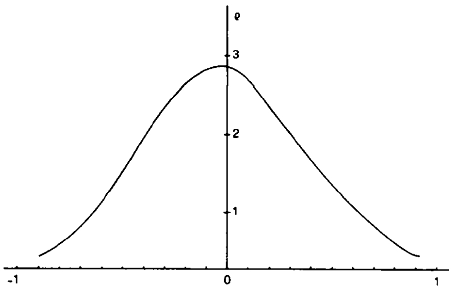


Fig. 7. Section of the theoretical electron density perpendicular to the triple bond through the midpoint (e Å^{-3} *vs* Å). The vertical direction is perpendicular to the ring plane; the left horizontal direction points toward the centre of the ring.

Table 9. *Deviations* ($Å \times 10^3$) *from least-squares planes*

Plane *A* is the best plane through C(5), C(6), C(11) and C(12), all weighted equally; planes *B* and *C* are the best planes through the C atoms of the two benzene rings. Direction cosines q_i ($\times 10^4$) are relative to the crystallographic axes; *D* is the origin-to-plane distance.

	Plane *A*			Plane *B*			Plane *C*		
	290 K	218 K	113 K	290 K	218 K	113 K	290 K	218 K	113 K
C(1)	53	46	40	−1	0	0	195	182	161
C(2)	98	87	81	1	1	−1	273	256	232
C(3)	99	90	91	−2	−1	0	266	253	238
C(4)	63	56	58	2	1	1	189	180	171
C(5)	1	1	2	27	29	26	50	50	48
C(6)	−1	−1	−2	66	65	59	11	12	11
C(7)	69	65	57	223	213	198	3	3	2
C(8)	100	97	86	296	286	270	1	1	2
C(9)	87	85	77	288	279	269	−3	−4	−4
C(10)	51	53	49	212	210	207	2	2	2
C(11)	1	1	2	75	76	80	29	25	23
C(12)	−1	−1	−2	32	35	38	63	59	51
C(13)	15	8	6	1	0	1	116	105	92
C(14)	17	13	13	−1	0	−1	110	104	96
C(15)	22	20	17	135	131	124	−4	−4	−3
C(16)	18	19	17	136	135	133	2	2	1
H(1)	74	77	57	24	35	24	222	217	180
H(2)	104	126	112	−19	16	8	308	321	286
H(3)	149	133	111	16	13	−10	340	320	279
H(4)	83	48	85	18	−10	21	204	169	195
H(7)	42	75	67	193	220	201	−30	9	10
H(8)	158	143	138	383	358	345	30	21	29
H(9)	131	103	101	361	325	323	17	−9	0
H(10)	60	71	51	223	230	215	17	26	9
q_a	3609	3610	3627	3492	3494	3485	3635	3649	3671
q_b	−5936	−5917	−5888	−6209	−6175	−6141	−5685	−5674	−5670
q_c	7128	7123	7113	6955	6964	6974	7314	7296	7262
D	4·3095	4·2960	4·2848	4·0819	4·0792	4·0746	4·4268	4·4088	4·3842

Dihedral angles	290 K	218 K	113 K
$A \wedge B$	178·0°	178·1°	178·1°
$A \wedge C$	178·2	178·3	178·5
$B \wedge C$	176·3	176·4	176·6

calculation with a STO 4-31G basis set (Hehre, Lathan, Ditchfield, Newton & Pople, 1973) of the electron density of the 1,5-cyclooctadiene-3,7-diyne system. The experimental values of the central-ring bond distances and angles of SDCD at 113 K, averaged assuming D_{2d} symmetry, were introduced in the calculation. As shown in Fig. 7, the theoretical electron density distribution around the triple bond at its centre is asymmetric, with slight accumulation of charge inside the ring. The greatest difference between the inner and the outer density occurs in the range 0·2–0·4 Å from the bond, and amounts to 0·27 e Å^{-3}. Although care must be taken in comparing observed densities with those calculated by quantum-mechanical methods (Ruysink & Vos, 1974*b*), the above mentioned theoretical results support our experimental findings.

Another feature of the difference density in the central ring plane is that the positive residues on the C_{sp}—C_{sp^2} bonds are systematically elongated outside the ring, with peak maxima 0·05–0·10 Å from the centre of the bonds. Whether this is evidence of slightly bent bonds is open to speculation.

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Structural Studies of Molybdenum–Amino Acid Complexes. The Crystal Structures of Bis-η-cyclopentadienyl-L-prolinatomolybdenum Hexafluorophosphate and Bis-η-cyclopentadienyl-L-leucinatomolybdenum Hexafluorophosphate

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The structures of the title compounds have been determined: (*a*) L-proline complex, monoclinic, $a = 9{\cdot}842$, $b = 9{\cdot}939$, $c = 8{\cdot}921$ Å, $\beta = 100{\cdot}22°$, space group $P2_1$, Mo $K\alpha$ radiation, Philips four-circle diffractometer data, 2919 reflexions, structure determined by Patterson methods and refined by least squares; final R 0·044; (*b*) leucine complex, monoclinic, $a = 6{\cdot}44$, $b = 10{\cdot}04$, $c = 30{\cdot}05$ Å, $\gamma = 94{\cdot}1°$, space group $P2_1/b$, Mo $K\alpha$ radiation, Hilger & Watts four-circle diffractometer data, 2135 reflexions, Patterson methods followed by least-squares refinement; final R 0·061. In each compound the $(\eta\text{-}C_5H_5)_2Mo$ moiety is chelated by the amino acid through O and N (proline Mo–O 2·108, Mo–N 2·255; leucine Mo–O 2·078, Mo–N 2·215 Å). The conformation of the $(\eta\text{-}C_5H_5)_2Mo$(prolinato) cation is consistent with the bulk of the prolinato ligand. In the leucine complex the shape and dimensions of the amino acid ligand are somewhat unsatisfactory possibly owing to disorder.

The presence of Mo in enzyme systems has promoted several crystallographic investigations of Mo–amino acid complexes. The bis-η-cyclopentadienyl compounds of the type $(\eta\text{-}C_5H_5)_2MoX_2$ provide a suitable system for the study of Mo^{IV} chemistry and previously we have reported the structures of compounds in which the bidentate chelating ligands X_2 were the amino acid anions of cysteine, sarcosine and glycine (Prout, Allison, Delbaere & Gore, 1972). It was demonstrated that Mo^{IV} complexed more readily with S than O and that the *N*-methyl substituent in sarcosine had little effect on the conformation of the complex. Here we report the structures of two further complexes, bis-η-cyclopentadienyl-L-prolinatomolybdenum(IV) hexafluorophosphate and bis-η-cyclopentadienylleucinatomolybdenum(IV) hexafluorophosphate–(?hydrate). The crystals were prepared by Dr M. L. H. Green and his co-workers.

(*a*) *Bis-η-cyclopentadienyl-L-prolinatomolybdenum hexafluorophosphate* (MoP)

$C_{15}H_{18}F_6MoNO_2P$, $M_r = 485{\cdot}22$, monoclinic, $a = 9{\cdot}842\,(3)$, $b = 9{\cdot}939\,(2)$, $c = 8{\cdot}921\,(2)$ Å, $\beta = 100{\cdot}22\,(4)°$, $U = 858{\cdot}8$ Å^3, $D_c = 1{\cdot}88$ g cm^{-3} for $Z = 2$. Space group $P2_1$, systematic extinctions $0k0$, $k = 2n + 1$. Mo $K\alpha$ radiation, graphite monochromator, $\mu = 8{\cdot}2$ cm^{-1}, crystal size $0{\cdot}18 \times 0{\cdot}06 \times 0{\cdot}70$ mm.

The cell dimensions were determined on a Philips PW 1100 diffractometer and refined by a least-squares fit over 25 reflexions. The intensities of a unique set of 3144 reflexions were measured in the range $\theta = 2$–$32°$ (total scan range 1·6°, scan rate 0·04° s^{-1}, ω–2θ scan mode) of which 225 with $I < \sigma(I)$ were discarded as unobserved. The variation in the absorption of X-rays by the crystal was investigated by ψ scans for 300