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ON THE ABSOLUTE CONFIGURATION OF ORGANOMETALLIC COMPOUNDS

VIII *. A COMPARISON OF THE STRUCTURAL CHARACTERISTICS OF RACEMIC AND OF $(-)_{578}$-$(\eta^5$-$C_5H_5)Mo(CO)_2SC(CH_3)NR$ WITH $R = CH[CH(CH_3)_2](C_6H_5)$ AND (*S*)-$CH[CH(CH_3)_2](C_6H_5)$

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Summary

The crystal structures of one of the diastereoisomers and of the racemic pairs having composition $(\eta^5$-$C_5H_5)Mo(CO)_2SC(CH_3)NR$ with $R = CH[CH(CH_3)_2]$-(C_6H_5) have been determined from single crystal X-ray diffraction data. The results that follow are given first for the active and then for the racemic crystal: Space group $P2_1$, $a = 9.366(2)$, $b = 16.199(3)$, $c = 12.722(1)$ Å, $\beta = 99.339(8)°$, $d(\text{calc.}) = 1.477$ gm cm^{-3} and $z = 4$ molecules/unit cell; Space group $P2_1/n$, $a = 9.111(2)$, $b = 12.774(4)$, $c = 16.465(4)$ Å, $\beta = 94.81(2)°$, $d(\text{calc.}) = 1.472$ gm cm^{-3} and $z = 4$ molecules/unit cell.

Refinement for the two crystals converged to $R(F) = 0.020$, $R_w(F) = 0.021$ and $R(F) = 0.073$, $R_w(F) = 0.075$. The Bijvoet test was applied to the enantiomorphic crystal and the configuration assigned is (*S*) for both the optically active carbon and the Mo site. Both compounds have an approximately square-pyramidal configuration around the Mo atom in which the thioamide ligand is bound through the S and the N atoms. This attachment of the thioamide ligand has only recently been structurally documented. The conformation of the molecules is nearly identical for all the compounds described in this study, as well as for similar species previously reported. Finally, the packing of the enantiomer and of the racemic pair is different. In spite of that, the density is nearly identical for the two substances.

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[*] For part VII see ref. 26.

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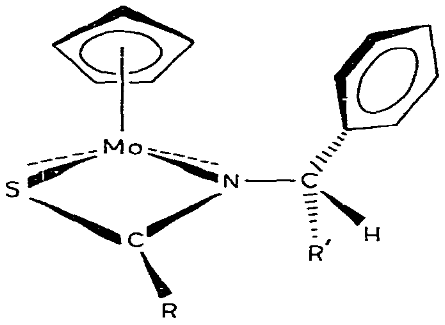
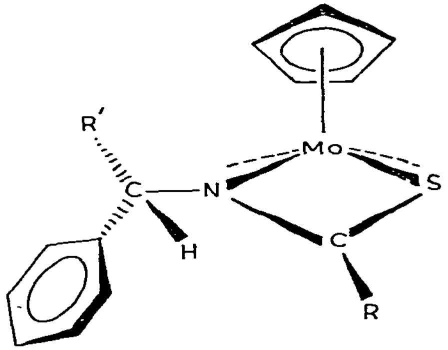
Introduction

Studies by Brunner and associates [1] have shown interesting correlations between the bulk of substituents R and R′ and the relative molar ratios of diastereoisomers (a) and (b) at equilibrium in solution. For the particular case of the thioacetamide prepared from (*S*)(—)-α phenylethylamine (R = R′ = CH_3), a toluene solution held at 40°C reaches equilibrium in a first order reaction ($\tau_{1/2}$ = 42 min) in which Ia and Ib interconvert by what seems to be a metal-centered, intramolecular rearrangement, caused by a 180° rotation of the entire thioacetamide ligand with respect to the $CpMo(CO)_2$ moiety [2—4]. Some time ago, we determined the crystal structure and the absolute configuration of diastereoisomer Ia which is the preferred species in toluene solutions (at 40°C, the ratio Ia/Ib equals 69/31) and is characterized by a (—) rotation at 578 nm [5]. It was shown [1] that a variation of the alkyl substituent, R′, at the (*S*)-$NCHR'(C_6H_5)$ induction center (from CH_3 to CH_2CH_3 and $CH(CH_3)_2$) leads to large changes in the equilibrium ratios Ia/Ib (69/31, 89/11 and 98/2, respectively). Thus, we decided to determine the crystal and molecular structure of the preferred diastereoisomer having the isopropyl substituent in order to investigate the effect of increased bulk on the structural parameters of the molecule and on its conformation and configuration.



(Ia)



(Ib)

We took advantage of two interesting opportunities afforded to us by the R′ = isopropyl derivative; i.e., the substance was available as a racemic mixture (III), having been prepared from the racemic amine, and it was available also as the pure diastereoisomer characterized by a (—) rotation at 578 nm (IIa). The latter crystals provided us with another opportunity; namely, there are two independent molecules in the asymmetric unit, which would permit us to comment on the usual, and nagging, question asked about solid state samples: "what is the effect of crystal packing on the conformation and configuration of the molecule?" Also, several investigators have documented instances in which the packing of a pure enantiomer in the solid is found to be nearly undistorted in crystals of the racemic mixture. That is, a crystal of the racemic mixture consists of two halves: one half is made up of one of the enantiomers with the same packing and conformational characteristics it has in the lattice of the pure enantiomer; the second half of the racemic crystal being the mirror image of the first half, as demanded by internal lattice symmetry. We were interested in making such a comparison in this case, having the relevant samples available for such tests.

Experimental

The details of the synthesis and physical properties of the preferred $(-)_{578}$ diastereoisomer and the racemic $(\eta^5\text{-}C_5H_5)Mo(CO)_2SC(CH_3)NR$ with $R = CH[CH(CH_3)_2]C_6H_5$ have been given elsewhere [7]. The two compounds will hereforth be referred to as IIa and III. Data collection for compounds IIa and III involved similar procedures. Intensity measurements were made on an ENRAF-NONIUS CAD-4 computer controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing is given in Table 1. Accurate cell constants determination and data collection were similar to those described elsewhere [8] and are, thus, not repeated here.

TABLE 1

CRYSTALLOGRAPHICALLY IMPORTANT DATA COLLECTION AND DATA PROCESSING INFORMATION FOR CRYSTALS OF IIa AND III

	Crystal IIa	Crystal III
Empirical formula	$MoSC_{19}NO_2H_{21}$	same
Molecular weight	423.37 g mol^{-1}	same
Cell constants	$a = 9.366(2)$ Å $b = 16.193(3)$ Å $c = 12.722(1)$ Å $\beta = 99.339(8)^\circ$	$a = 9.111(2)$ Å $b = 12.774(4)$ Å $c = 16.465(4)$ Å $\beta = 94.81(2)^\circ$
Unit cell volume	$V = 1904.0$ Å^3	$V = 1909.7$ Å^3
Space group	$P2_1$	$P2_1/n$
Number of molecules in asymmetric unit	2	1
Density [a]	ρ(calcd.) = 1.477 g cm^{-3}	1.472 g cm^{-3}
Absorption coefficient (Mo-K_α)	$\mu = 7.9$ cm^{-1}	same
Radiation used for data collection	Mo-K_α ($\lambda = 0.71069$ Å)	same
Scanning range for 2θ	$5.00^\circ < 2\theta < 60.0^\circ$	$4.00^\circ < 2\theta < 70.0^\circ$
Standards for intensity control	[2,4,3 and 1,4,6]	[5,4,3 and 0,4,$\bar{1}\bar{0}$]
Scan width for each reflection	$\Delta\Theta = (1.0 + 0.40 \tan\theta)^\circ$	$\Delta\Theta = (1.17 + 0.35 \tan\theta)^\circ$
Maximum scan time	5 minutes	4 minutes
Minimum number of counts above background for each reflection	2000	same
Scan technique	θ—2θ	same
Total number of reflections collected [b]	8938	6801
Number of contributing reflection in the last least-squares [c]	6620	5067
Number of variables	601	301
Weighting scheme	$w = 1/\sigma^2(F_0)$	same
Final R(F) [d]	0.020	0.073
Final R_w(F) [e]	0.021	0.075

[a] The density was not measured because in both cases only one crystal was available (which was used in determining the sign of the optical rotation of crystal IIa at the end of data collection). [b] For crystal IIa a total of 8938 reflections were collected of which 4264 having $I > 3\sigma(I)$ were classified as "observed" with the remaining 4674 being turned "less-thans". For the second crystal, 3390 reflections were classified "observed" and 3411 "less thans". [c] 4264 "observed" and 2356 "less-thans", for which $|F_c| > |F_0|$ for crystal IIa and 3390 "observed" and 1677 "less-thans" for crystal III. [d] $R(F) = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [e] $R_w(F) = [\Sigma w||F_0| - |F_c||^2/\Sigma_0|^2]^{1/2}$.

Solution and refinement

Data decoding was accomplished using a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factors amplitudes, $|F_0|$. No corrections for absorption were made due to the

TABLE 2

FINAL POSITIONAL PARAMETERS OF THE NON-HYDROGEN ATOMS FOR CRYSTAL IIa

Atom [a]	X	Y	Z
Mo	−0.34448(3) [b]	0.00000 [c]	−0.11625(2)
	−0.09909(3)	−0.31419(2)	−0.40792(2)
S	−0.20847	0.08808(6)	0.02896(6)
	0.06841(9)	−0.21072(5)	−0.30613(6)
N	−0.4743(2)	0.0552(1)	−0.0029(2)
	−0.1321(2)	−0.1828(1)	−0.4587(2)
O(1)	−0.1886(3)	0.1123(2)	−0.2608(2)
	0.1930(3)	−0.3999(2)	−0.4279(2)
O(2)	−0.5656(3)	0.0606(2)	−0.3109(2)
	−0.1121(3)	−0.3616(1)	−0.6470(2)
C(1)	−0.3710(4)	−0.1323(2)	−0.0379(3)
	−0.3201(3)	−0.3149(2)	−0.3335(2)
C(2)	−0.4227(4)	−0.1345(2)	−0.1502(3)
	−0.3199(3)	−0.3811(2)	−0.4056(2)
C(3)	−0.3017(4)	−0.1190(2)	−0.2014(2)
	−0.2048(4)	−0.4344(2)	−0.3651(3)
C(4)	−0.1783(4)	−0.1054(2)	−0.1228(3)
	−0.1313(4)	−0.4003(2)	−0.2687(3)
C(5)	−0.2250(4)	−0.1154(2)	−0.0228(2)
	−0.2052(4)	−0.3257(2)	−0.2502(2)
C(6)	−0.2460(3)	0.0716(2)	−0.2044(2)
	0.0858(4)	−0.3663(2)	−0.4193(2)
C(7)	−0.4900(3)	0.0386(2)	−0.2340(2)
	−0.1095(3)	−0.3409(2)	−0.5599(2)
C(8)	−0.3776(3)	0.0942(2)	0.0644(2)
	−0.0353(3)	−0.1438(2)	−0.3914(2)
C(9)	−0.4016(4)	0.1420(2)	0.1612(2)
	−0.0068(4)	−0.0520(2)	−0.3835(2)
C(10)	−0.6292(3)	0.0565(2)	0.0081(2)
	−0.2327(3)	−0.1376(2)	−0.5418(2)
C(11)	−0.7231(3)	0.0971(2)	−0.0869(2)
	−0.1960(3)	−0.1503(2)	−0.6543(2)
C(12)	−0.8776(4)	0.1060(3)	−0.0674(3)
	−0.2952(4)	−0.0958(3)	−0.7315(2)
C(13)	−0.6617(4)	0.1820(2)	−0.1083(2)
	−0.0389(4)	−0.1333(3)	−0.6598(3)
C(14)	−0.6777(3)	−0.0297(2)	0.0344(2)
	−0.3870(3)	−0.1578(2)	−0.5321(2)
C(15)	−0.7333(4)	−0.0879(2)	−0.0428(2)
	−0.4541(4)	−0.2305(2)	−0.5746(2)
C(16)	−0.7750(4)	−0.1657(2)	−0.0146(3)
	−0.5936(4)	−0.2502(2)	−0.5591(3)
C(17)	−0.7636(5)	−0.1875(2)	0.0912(3)
	−0.6681(4)	−0.1983(3)	−0.5014(3)
C(18)	−0.7102(5)	−0.1316(3)	0.1692(3)
	−0.6047(4)	−0.1264(3)	−0.4620(3)
C(19)	−0.6686(4)	−0.0531(2)	0.1414(2)
	−0.4656(4)	−0.1046(2)	−0.4770(2)

[a] First entry is for molecule 1, second entry for molecule 2 in this and succeeding tables. [b] Numbers in parentheses are the estimated standard deviations in the least significant digits in this and succeeding tables. [c] Arbitrarily assigned.

low value of the absorption coefficient ($\mu = 7.9\ \mathrm{cm}^{-1}$). Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{\mathrm{TOT}} + 2\Sigma I_{\mathrm{BG}}$. Standard deviations in the structure factor amplitudes, $\sigma(|F_0|)$, were estimated as $\sigma(|F_0|) = \sigma(I)/2(Lp)|F_0|$. All data processing and calculations were carried out with the X-ray '72 system of programs [9].

A three-dimensional Patterson map was computed for both compounds and the positions of the molybdenum atoms were determined. All the remaining non-hydrogen atoms were easily found from successive difference Fourier maps and refined. Conversion to anisotropic thermal parameters was then accomplished. At this stage hydrogen atoms were added at theoretically calculated positions (C—H 0.95 Å). Further anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogens yielded the following final agreement factors: $R(F) = 0.02$ and 0.07 for compounds IIa and III, respectively. The higher agreement factor of compound III is due to the poor quality of the crystals. The function minimized during all the least-squares refinements was $\Sigma w(|F_0| - |F_0|)^2$, where w, the weighting factors, were $[\sigma(|F_0|)]^{-2}$. The atomic scattering curves of Cromer and Mann [10] were used for the non-hydrogen atoms, and for the hydrogen atoms, the curve of Stewart et al. [11], was used. Corrections for the real and imaginary terms of the anomalous dispersion for Mo and S were applied for compound IIa. (The sign of $\Delta f''$ was reversed after the absolute configuration determination — see next paragraph.) For III only the real part of the anomalous dispersion for Mo and S was used. The values used for these corrections were those given in the International Tables for X-ray Crystallography [12]. The estimated standard deviations were

TABLE 3

FINAL POSITIONAL PARAMETERS OF THE NON-HYDROGEN ATOMS FOR CRYSTAL III

Atom	*X*	*Y*	*Z*
Mo	0.08691(8)	0.23365(5)	0.19945(3)
S	—0.0790(3)	0.3641(2)	0.2586(1)
N	—0.1177(7)	0.2751(5)	0.1229(3)
O(1)	0.0612(9)	0.1324(6)	0.3708(3)
O(2)	0.0114(10)	—0.0015(5)	0.1722(4)
C(1)	0.3323(11)	0.2028(7)	0.1964(4)
C(2)	0.3193(10)	0.2961(8)	0.2412(4)
C(3)	0.2582(12)	0.3728(7)	0.1864(5)
C(4)	0.2341(11)	0.3260(8)	0.1104(5)
C(5)	0.2742(11)	0.2224(8)	0.1150(5)
C(6)	0.0697(11)	0.1709(7)	0.3073(5)
C(7)	0.0339(11)	0.0873(7)	0.1796(4)
C(8)	—0.1840(10)	0.3410(6)	0.1656(4)
C(9)	—0.3277(12)	0.3961(8)	0.1475(6)
C(10)	—0.1822(9)	0.2411(6)	0.0401(4)
C(11)	—0.2362(9)	0.1277(6)	0.0408(4)
C(12)	—0.3194(16)	0.1014(10)	—0.0430(6)
C(13)	—0.3331(12)	0.1067(8)	0.1089(6)
C(14)	—0.0734(9)	0.2675(6)	—0.0209(3)
C(15)	0.0286(10)	0.1971(7)	—0.0451(4)
C(16)	0.1304(11)	0.2261(9)	—0.0986(5)
C(17)	0.1289(13)	0.3294(10)	—0.1298(5)
C(18)	0.0279(13)	0.3983(9)	—0.1064(5)
C(19)	—0.0734(11)	0.3690(7)	—0.0535(4)

TABLE 4

FINAL POSITIONAL PARAMETERS AND THERMAL PARAMETERS ($\times 10^3$) OF THE HYDROGEN ATOMS FOR CRYSTAL IIa

Atom	X	Y	Z	U_{iso}
H(1)	−0.439(3)	−0.133(2)	0.007(2)	75(11)
	−0.388(3)	−0.271(2)	−0.345(2)	79(11)
H(2)	−0.522(4)	−0.144(2)	−0.188(2)	97(13)
	−0.396(4)	−0.388(2)	−0.468(2)	82(11)
H(3)	−0.294(3)	−0.119(2)	−0.271(2)	66(10)
	−0.178(4)	−0.492(3)	−0.393(2)	98(12)
H(4)	−0.074(3)	−0.093(2)	−0.137(2)	71(10)
	−0.033(3)	−0.420(2)	−0.227(2)	68(10)
H(5)	−0.157(3)	−0.108(2)	0.038(2)	56(10)
	−0.168(3)	−0.287(2)	−0.196(2)	74(10)
H(91)	−0.444(4)	0.109(2)	0.219(2)	89(12)
	−0.94(4)	−0.015(3)	−0.376(3)	123(15)
H(92)	−0.478(3)	0.181(2)	0.146(2)	66(10)
	0.019(3)	−0.029(2)	−0.449(2)	64(10)
H(93)	−0.319(3)	0.161(2)	0.192(2)	58(10)
	0.067(4)	−0.039(2)	−0.331(3)	85(12)
H(10)	−0.639(3)	0.090(2)	0.067(2)	42(8)
	−0.226(3)	−0.077(2)	−0.525(2)	50(9)
H(11)	−0.722(3)	0.065(2)	−0.149(2)	45(8)
	−0.218(3)	−0.207(1)	−0.674(2)	42(8)
H(121)	−0.881(4)	0.139(2)	−0.006(3)	101(13)
	−0.266(5)	−0.034(2)	−0.716(3)	123(15)
H(122)	−0.917(5)	0.055(3)	−0.054(3)	134(16)
	−0.389(5)	−0.088(3)	−0.726(3)	130(16)
H(123)	−0.931(4)	0.120(2)	−0.126(3)	98(13)
	−0.273(4)	−0.096(2)	−0.809(3)	116(15)
H(131)	−0.562(3)	0.186(2)	−0.117(2)	68(9)
	0.011(3)	−0.158(2)	−0.610(2)	69(10)
H(132)	−0.664(3)	0.214(2)	−0.044(2)	77(11)
	−0.021(5)	−0.062(3)	−0.658(3)	141(17)
H(133)	−0.711(4)	0.207(2)	−0.175(2)	93(12)
	−0.021(4)	−0.141(2)	−0.725(3)	86(12)
H(15)	−0.741(3)	−0.080(2)	−0.119(2)	68(10)
	−0.407(3)	−0.271(2)	−0.619(2)	53(9)
H(16)	−0.830(4)	−0.210(2)	−0.064(3)	104(14)
	−0.646(4)	−0.299(2)	−0.594(3)	112(14)
H(17)	−0.802(4)	−0.240(2)	0.111(3)	96(13)
	−0.766(4)	−0.220(2)	−0.481(3)	116(14)
H(18)	−0.712(4)	−0.144(2)	0.236(3)	94(12)
	−0.640(4)	−0.091(2)	−0.429(2)	92(12)
H(19)	−0.632(3)	−0.002(2)	0.199(2)	75(10)
	−0.415(3)	−0.053(2)	−0.453(2)	78(11)

computed from the inverse matrix of the final, full-matrix, least-squares cycle. Final positional and thermal parameters for compound IIa are presented in Tables 2, 4 and 6, and for compound III in Tables 3, 5 and 7. Interatomic distances and angles of both compounds are given in Tables 8 and 9. The equations of the least-squares planes through selected groups of atoms are given in Table 10 and torsional angles are presented in Table 11. The stereo drawings for compound IIa (Figs. 1, 2, and 3) and the packing diagram for compound III (Fig. 4) were obtained with Johnson's ORTEP2 [13]. Final observed and calculated structure factors are available from the authors.

TABLE 5

FINAL POSITIONAL PARAMETERS OF THE HYDROGEN ATOMS FOR CRYSTAL III

Atom	X	Y	Z
H(1)	0.352(18)	0.137(12)	0.180(9)
H(2)	0.309(17)	0.321(12)	0.311(9)
H(3)	0.233(9)	0.437(6)	0.196(4)
H(4)	0.181(15)	0.370(10)	0.071(8)
H(5)	0.251(15)	0.153(10)	0.081(8)
H(91)	—0.311(15)	0.433(11)	0.109(8)
H(92)	—0.397(14)	0.341(11)	0.138(8)
H(93)	—0.370(12)	0.433(9)	0.190(7)
H(10)	—0.265(8)	0.281(6)	0.028(4)
H(11)	—0.129(10)	0.082(7)	0.033(5)
H(121)	—0.397(12)	0.164(8)	—0.043(6)
H(122)	—0.231(11)	0.108(7)	—0.086(6)
H(123)	—0.328(13)	0.031(9)	—0.045(6)
H(131)	—0.279(10)	0.121(7)	0.159(6)
H(132)	—0.422(13)	0.153(9)	0.100(6)
H(133)	—0.368(11)	0.040(8)	0.115(6)
H(15)	—0.136(8)	.0.421(6)	—0.037(4)
H(16)	0.034(11)	0.471(7)	—0.114(5)
H(17)	0.213(9)	0.344(6)	—0.161(4)
H(18)	0.218(12)	0.184(8)	—0.111(6)
H(19)	0.034(9)	0.125(6)	—0.020(4)

Determination of the absolute configuration of IIa

When refinement converged, the molecular configuration was the mirror image of that given in Fig. 1, in which the numbering system employed in the crystallographic analysis is indicated. At this stage, structure-factor tables were computed using the two possible configurations (xyz and $\bar{x}\bar{y}\bar{z}$) and a set of 9 reflections (see Table 12) was chosen for which the two Friedel pairs (hkl and $\bar{h}\bar{k}\bar{l}$) showed marked differences. The scanning routine [14] MODE = —1 was used and each of the 9 reflections was measured 4 separate times in the order (hkl, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$, hkl, hkl, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}\bar{l}$ and hkl). The measured values listed were averaged over the four independent measurements and the results consistently showed that the correct absolute configuration was the mirror image of the refined enantiomer, chosen during the initial solution of the structure. The coordinates given in Table 2 correspond to those of the correct enantiomer and Figs. 1, 2 and 3 also depict the molecule in its correct absolute configuration. The absolute configuration thus obtained shows C(10), the optically active carbon derived from the parent optically active amine, in an (*S*) configuration which is the known configuration of the amine used in the synthesis of the ligand [7]. Using the extension of the *R*, *S* system [15] to polyhapto ligands in organometallic complexes [16], the priority sequence of the ligands is $C_5H_5 > S > N > C(CO)$. Thus, according to the sequence rule of the *R*, *S* system and the line of sight convention [17], the configuration at the Mo atom is (*S*). As in the case of the previously studied compound of $(-)_{578}$-$(\eta^5$-$C_5H_5)Mo(CO)_2$-$SC(CH_3)NR^*$ where R = (*S*)-$CH(CH_3)(C_6H_5)$[5] the asymmetric (*S*) center at the carbon of the amine induces an (*S*) configuration at the labile metal.

(Continued on p. 69)

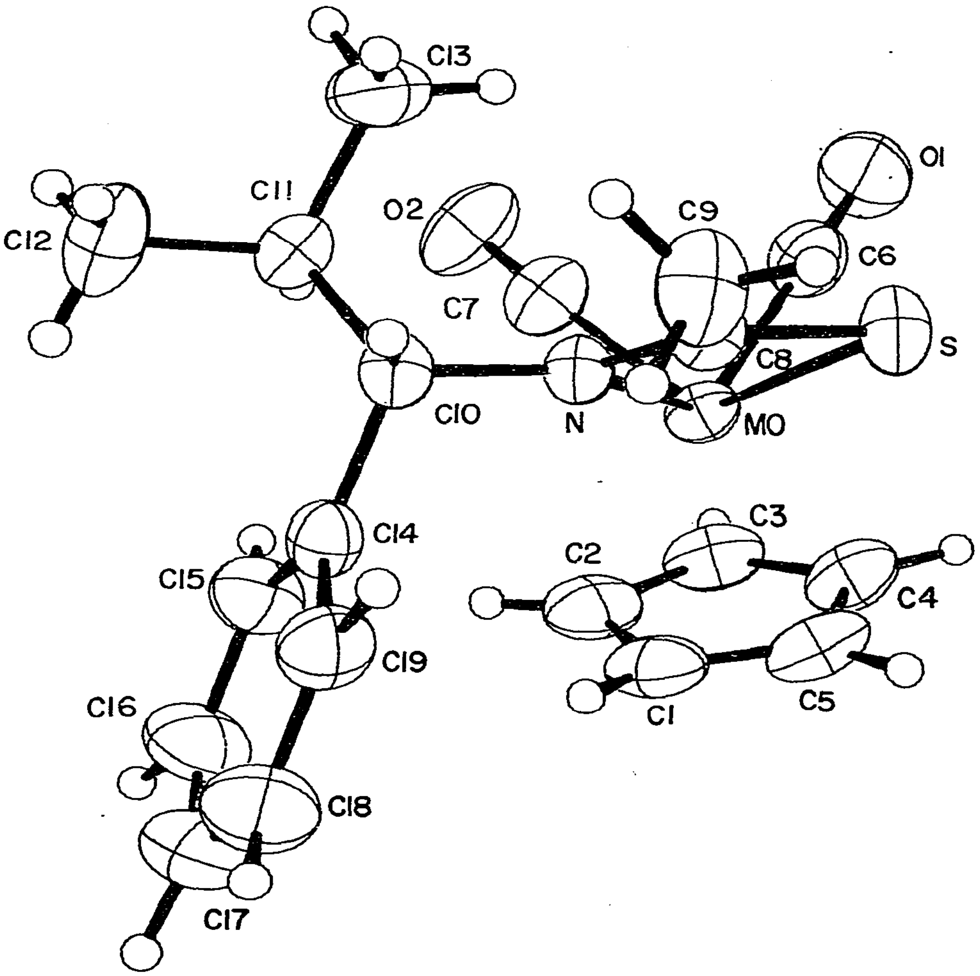


Fig. 1. A general view of compound IIa in its correct absolute configuration showing the labelling scheme used in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms.

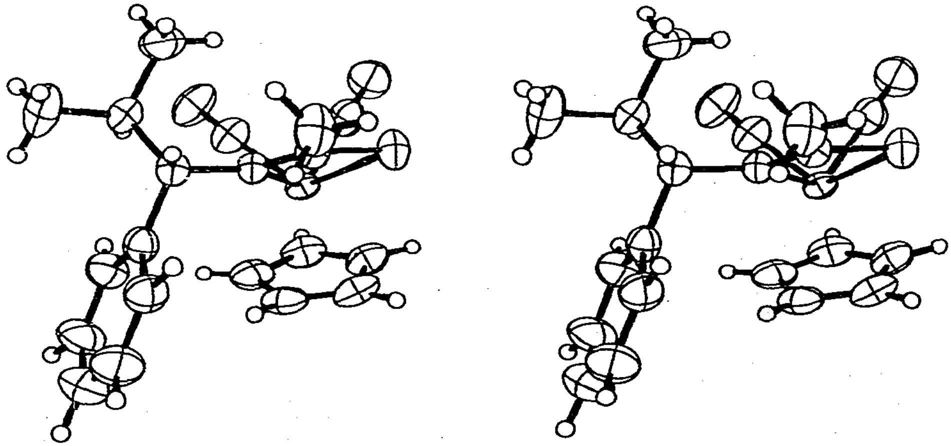


Fig. 2. A stereo pair of the molecule in its correct absolute configuration.

TABLE 6

THERMAL PARAMETERS ($\times 10^3$)[a] OF THE NON-HYDROGEN ATOMS FOR CRYSTAL IIa

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	41.4(1)	34.4(1)	32.1(1)	7.2(1)	8.2(1)	—0.5(1)
	42.1(1)	33.2(1)	33.4(1)	1.2(1)	7.3(1)	1.8(1)
S	34.5(4)	57.0(5)	51.9(5)	—2.4(4)	5.8(4)	—9.6(4)
	46.3(5)	49.8(5)	37.3(4)	1.3(4)	—4.7(4)	—1.3(4)
N	32(1)	35(1)	33(1)	1(1)	5(1)	—4(1)
	36(1)	34(1)	31(1)	—2(1)	4(1)	0(1)
O(1)	71(2)	91(2)	72(2)	—4(2)	25(1)	31(2)
	57(2)	66(2)	98(2)	19(1)	10(1)	—7(2)
O(2)	76(2)	94(2)	40(1)	32(2)	—5(1)	—1(1)
	95(2)	63(2)	41(1)	20(1)	11(1)	—10(1)
C(1)	75(2)	34(2)	66(2)	15(2)	25(2)	11(2)
	60(2)	49(2)	56(2)	0(2)	28(2)	3(2)
C(2)	80(3)	31(2)	65(2)	6(2)	8(2)	—7(2)
	50(4)	46(2)	60(2)	—6(2)	16(2)	3(2)
C(3)	84(3)	45(2)	45(2)	17(2)	18(2)	—6(2)
	70(2)	37(2)	68(2)	—3(2)	20(2)	10(2)
C(4)	64(2)	52(2)	57(2)	26(2)	17(2)	—3(2)
	71(3)	59(2)	51(2)	—1(2)	12(2)	18(2)
C(5)	77(3)	50(2)	50(2)	28(2)	6(2)	7(2)
	73(2)	48(2)	44(2)	—10(2)	22(2)	2(2)
C(6)	48(2)	60(2)	49(2)	7(2)	12(2)	0(2)
	56(2)	42(4)	50(2)	—1(2)	4(2)	2(2)
C(7)	55(2)	55(2)	40(2)	12(2)	10(2)	—10(2)
	54(2)	36(2)	48(2)	11(2)	12(2)	1(1)
C(8)	38(2)	41(2)	38(2)	2(1)	6(1)	—1(1)
	38(2)	40(2)	33(2)	—11(1)	8(1)	—1(1)
C(9)	48(2)	74(2)	48(2)	0(2)	3(2)	—27(2)
	57(2)	43(2)	54(2)	—11(2)	—3(2)	—6(2)
C(10)	35(2)	38(2)	34(1)	1(1)	6(1)	—8(1)
	38(2)	30(1)	37(1)	0(1)	2(1)	2(1)
C(11)	40(2)	44(2)	40(2)	8(2)	4(1)	—1(1)
	45(2)	54(2)	33(1)	—1(2)	5(1)	4(1)
C(12)	42(2)	104(3)	65(2)	17(2)	4(2)	6(2)
	82(3)	95(3)	41(2)	16(3)	3(2)	24(2)
C(13)	72(2)	42(2)	62(2)	4(2)	—3(2)	6(2)
	55(2)	142(4)	52(2)	—8(3)	20(2)	16(3)
C(14)	36(2)	48(2)	38(2)	1(1)	8(1)	0(1)
	34(2)	41(2)	33(1)	4(1)	2(1)	3(1)
C(15)	61(2)	51(2)	46(2)	—8(2)	4(2)	—1(2)
	45(2)	49(2)	48(2)	—2(2)	5(2)	0(2)
C(16)	78(3)	50(2)	78(3)	—21(2)	3(2)	0(2)
	45(2)	75(3)	62(2)	—12(2)	1(2)	5(2)
C(17)	78(3)	56(3)	97(3)	—16(2)	11(3)	19(2)
	39(2)	107(4)	66(2)	—2(2)	8(2)	13(2)
C(18)	84(3)	79(3)	57(2)	—2(3)	18(2)	23(2)
	57(3)	94(3)	72(3)	20(2)	23(2)	—5(2)
C(19)	54(2)	58(2)	42(2)	2(2)	4(2)	8(2)
	49(2)	61(2)	52(2)	11(2)	4(2)	—3(2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2b_{23}kl)]$ and $U_{ij} = \beta_{ij}/2\pi^2 a_i^\star a_j^\star$.

TABLE 7

THERMAL PARAMETERS ($\times 10^3$) OF THE NON-HYDROGEN ATOMS FOR CRYSTAL III

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	50.5(4)	44.0(3)	28.1(2)	−0.7(3)	−10.8(2)	−3.3(2)
S	75(2)	58(1)	37(1)	0(1)	1(1)	−12(1)
N	44(4)	44(3)	31(2)	3(3)	−8(2)	0(2)
O(1)	110(6)	103(5)	42(3)	−16(5)	−16(3)	21(3)
O(2)	133(7)	44(3)	91(5)	4(4)	−57(5)	−1(3)
C(1)	69(6)	77(6)	36(3)	12(5)	−7(4)	−4(4)
C(2)	62(6)	82(6)	38(3)	−19(5)	−18(4)	0(4)
C(3)	74(7)	56(5)	62(5)	−13(5)	−10(5)	−1(4)
C(4)	59(6)	76(6)	46(4)	−9(5)	−14(4)	5(4)
C(5)	63(6)	86(6)	40(4)	5(5)	−14(4)	−4(4)
C(6)	69(6)	60(5)	43(4)	−14(4)	−10(4)	0(3)
C(7)	75(7)	50(4)	46(4)	6(4)	−30(4)	2(3)
C(8)	57(6)	46(4)	38(3)	2(4)	−4(3)	−2(3)
C(9)	64(7)	77(7)	80(6)	24(6)	0(5)	−10(5)
C(10)	45(5)	48(4)	35(3)	1(3)	−14(3)	1(3)
C(11)	50(5)	51(4)	40(3)	−10(4)	−13(3)	3(3)
C(12)	96(10)	76(7)	57(5)	−30(7)	−32(6)	−2(5)
C(13)	67(7)	70(6)	65(5)	−19(5)	−6(5)	12(4)
C(14)	50(5)	46(3)	26(2)	−7(3)	−12(3)	1(2)
C(15)	56(6)	64(5)	34(3)	−11(4)	−6(3)	−8(3)
C(16)	62(6)	102(8)	41(4)	−15(6)	−5(4)	−19(4)
C(17)	81(8)	115(9)	35(4)	−45(7)	−6(4)	2(5)
C(18)	85(8)	81(7)	50(5)	−23(6)	−18(5)	17(4)
C(19)	68(6)	57(5)	41(3)	−10(4)	−11(4)	8(3)

TABLE 8

BOND DISTANCES (Å) FOR CRYSTALS IIa AND III

	Crystal IIa		Crystal III
	Molecule 1	Molecule 2	
Mo—S	2.5113(8)	2.5072(9)	2.501(2)
Mo—N	2.220(2)	2.231(2)	2.225(6)
Mo—C(1)	2.393(3)	2.412(3)	2.275(10)
Mo—C(2)	2.317(3)	2.340(3)	2.313(9)
Mo—C(3)	2.278(3)	2.289(3)	2.387(10)
Mo—C(4)	2.321(4)	2.312(4)	2.382(9)
Mo—C(5)	2.393(3)	2.386(3)	2.294(9)
Mo—C(6)	1.947(3)	1.953(3)	1.966(8)
Mo—C(7)	1.957(3)	1.968(3)	1.951(8)
S—C(8)	1.719(3)	1.718(3)	1.760(7)
N—C(8)	1.303(3)	1.304(3)	1.281(10)
C(8)—C(9)	1.503(4)	1.511(4)	1.494(14)
N—C(10)	1.480(4)	1.489(3)	1.503(8)
C(10—C(11)	1.523(4)	1.539(4)	1.531(11)
C(10)—C(14)	1.522(4)	1.507(4)	1.507(10)
C(11)—C(12)	1.514(5)	1.520(5)	1.555(13)
C(11)—C(13)	1.531(5)	1.510(5)	1.508(13)
C(1)—C(2)	1.433(5)	1.412(5)	1.412(13)
C(2)—C(3)	1.419(6)	1.411(5)	1.415(13)
C(3)—C(4)	1.417(5)	1.417(5)	1.388(12)
C(4)—C(5)	1.420(5)	1.431(5)	1.372(14)
C(5)—C(1)	1.377(5)	1.393(4)	1.421(11)
C(14)—C(15)	1.400(4)	1.400(4)	1.376(12)
C(15)—C(16)	1.382(5)	1.390(5)	1.383(13)

TABLE 8 (continued)

	Crystal IIa		Crystal III
	Molecule 1	Molecule 2	
C(16)—C(17)	1.379(6)	1.378(6)	1.416(17)
C(17)—C(18)	1.376(6)	1.364(6)	1.353(17)
C(18)—C(19)	1.393(6)	1.393(6)	1.373(14)
C(19)—C(14)	1.401(4)	1.394(5)	1.403(11)
C(6)—O(1)	1.167(4)	1.163(4)	1.165(10)
C(7)—O(2)	1.167(3)	1.154(4)	1.158(11)
C(1)—H(1)	0.92(3)	0.95(3)	0.90(16)
C(2)—H(2)	0.98(3)	0.98(3)	1.20(14)
C(3)—H(3)	0.90(3)	1.05(4)	0.87(8)
C(4)—H(4)	1.04(3)	1.04(3)	0.96(13)
C(5)—H(5)	0.93(3)	0.96(3)	1.06(13)
C(9)—H(91)	1.04(3)	1.03(4)	0.81(14)
C(9)—H(92)	0.95(3)	0.97(3)	0.95(12)
C(9)—H(93)	0.86(3)	0.91(3)	0.96(11)
C(10)—H(10)	0.94(2)	1.00(3)	0.92(8)
C(11)—H(11)	0.95(2)	0.97(2)	1.15(9)
C(12)—H(121)	0.95(4)	1.04(4)	1.07(11)
C(12)—H(122)	0.93(5)	0.90(5)	1.12(10)
C(12)—H(123)	0.86(3)	1.04(4)	0.90(11)
C(13)—H(131)	0.96(3)	0.82(3)	0.95(11)
C(13)—H(132)	0.98(3)	1.16(5)	1.01(11)
C(13)—H(133)	0.98(3)	0.88(3)	0.91(10)
C(15)—H(15)	0.97(3)	1.01(3)	1.00(8)
C(16)—H(16)	1.04(4)	1.00(4)	1.00(8)
C(17)—H(17)	0.97(4)	1.05(4)	0.98(8)
C(18)—H(18)	0.88(3)	0.81(4)	0.93(9)
C(19)—H(19)	1.13(3)	0.99(3)	0.93(7)

TABLE 9

ANGLES (°) FOR CRYSTALS IIa AND III

	Crystal IIa		Crystal III
	Molecule 1	Molecule 2	
S—Mo—N	63.84(6)	63.77(6)	63.7(1)
S—Mo—C(6)	81.63(9)	80.74(9)	79.8(3)
S—Mo—C(7)	126.1(1)	125.6(1)	123.6(3)
N—Mo—C(7)	88.9(1)	86.7(1)	87.1(3)
N—Mo—C(6)	119.7(1)	118.3(1)	118.8(3)
C(6)—Mo—C(7)	72.8(1)	74.6(1)	73.9(3)
Mo—S—C(8)	81.2(1)	81.5(1)	81.5(3)
S—C(8)—C(9)	120.7(2)	120.2(2)	120.0(6)
S—C(8)—N	111.8(2)	111.8(2)	109.9(6)
N—C(8)—C(9)	127.4(3)	128.0(2)	130.2(7)
Mo—N—C(10)	135.7(2)	135.8(2)	133.6(5)
Mo—N—C(8)	103.1(2)	102.8(2)	104.9(4)
C(8)—N—C(10)	121.2(2)	121.4(2)	121.5(6)
N—C(10)—C(11)	112.3(2)	112.5(2)	111.6(5)
N—C(10)—C(14)	109.9(2)	109.8(2)	108.1(6)
C(11)—C(10)—C(14)	114.5(2)	114.1(2)	116.6(6)
C(10—C(11)—C(12)	110.8(3)	108.5(3)	109.3(7)
C(10)—C(11)—C(13)	110.0(2)	112.6(2)	112.5(7)
C(12)—C(11)—C(13)	109.8(3)	111.3(3)	110.4(8)
C(10)—C(14)—C(15)	123.5(3)	121.8(3)	122.9(7)

TABLE 9 (continued)

	Crystal IIa		Crystal III
	Molecule 1	Molecule 2	
C(10)—C(14)—C(19)	119.2(3)	119.9(3)	118.8(7)
C(2)—C(1)—C(5)	108.1(3)	108.4(3)	107.6(8)
C(1)—C(2)—C(3)	106.7(3)	108.0(3)	107.2(7)
C(2)—C(3)—C(4)	108.9(3)	108.3(3)	107.5(8)
C(3)—C(4)—C(5)	106.3(3)	106.9(3)	110.1(7)
C(4)—C(5)—C(1)	110.0(3)	108.3(3)	107.4(8)
C(15)—C(14)—C(19)	117.2(3)	118.2(3)	118.2(7)
C(14)—C(15)—C(16)	121.3(3)	120.7(3)	121.0(8)
C(15)—C(16)—C(17)	120.4(3)	120.3(4)	119.6(1.0)
C(16)—C(17)—C(18)	119.8(4)	119.2(4)	119.3(1.0)
C(17)—C(18)—C(19)	120.1(3)	121.8(4)	120.9(1.0)
C(18)—C(19)—C(14)	119.6(3)	121.2(3)	121.0(9)
Mo—C(6)—O(1)	177.2(3)	177.4(3)	178.8(8)
Mo—C(7)—O(2)	172.8(3)	175.5(3)	174.7(8)

TABLE 10

LEAST-SQUARES PLANES (IN ORTHOGONAL Å SPACE) AND DEVIATIONS OF ATOMS FROM THESE PLANES (IN Å)

Crystal IIa

(a) Plane based on C(1), C(2), C(3), C(4) and C(5).

$-0.2061x \quad +0.9785y \quad +0.0083z \quad = \quad -1.4005$

$0.6920x \quad +0.5142y \quad -0.5066z \quad = \quad -2.0943$

C(1)	0.005,	−0.0047	C(2)	0.0053	0.0067
C(3)	−0.0090,	−0.0061	C(4)	0.0092	0.0032
C(5)	−0.0060,	0.0009	Mo	2.0039	2.0133

(b) Plane based on C(14), C(15), C(16), C(17), C(18) and C(19).

$0.9404x \quad -0.3399y \quad -0.0103z \quad = \quad -5.8837$

$0.2381x \quad -0.4758y \quad +0.8467z \quad = \quad -5.0565$

C(14)	0.0062,	0.0150	C(15)	−0.0028	−0.0054
C(16)	−0.0009	−0.0078	C(17)	0.0010	0.0112
C(18)	0.0026	−0.0013	C(19)	−0.0063	−0.0118

(c) Plane Based on C(6), C(7), S and N.

$-0.2052x \quad +0.9730y \quad -0.1056z \quad = \quad 1.7734$

$-0.7447x \quad -0.4020y \quad +0.5328z \quad = \quad -1.6431$

C(6)	0.0120	−0.0204	C(7)	−0.0120	0.0205
S	−0.0111	0.0193	N	0.0111	−0.0194
Mo	−1.0063	1.0238			

(d) Plane based on Mo, S, N and C(8).

$-0.0855x \quad +0.8118y \quad -0.5777z \quad = \quad 1.1074$

$-0.7559x \quad +0.1097y \quad +0.6454z \quad = \quad -3.8063$

Mo	−0.0091	0.0078	S	0.0123	−0.0106
N	0.0186	−0.0160	C(8)	−0.0218	0.0188
C(9)	−0.0592	0.0558	C(10)	0.0822	−0.0265

(e) Plane based on N, C(10), C(11) and C(12).

$0.1071x \quad +0.8967y \quad +0.4295z \quad = \quad 0.2721$

$0.6266x \quad +0.7668y \quad +0.1391z \quad = \quad -3.2846$

N	0.0395	0.0321	C(10)	−0.0406	−0.0344
C(11)	−0.0371	−0.0284	C(12)	0.0382	0.0307

TABLE 10 (continued)

(f) Equations of lines in orthogonal Å space
(α) Line defined by C(10) and C(11).

L(1) = I = (6.2519) + (0.4487)T
L(2) = J = (−1.2435) + (−0.4310)T
L(3) = K = (0.4946) + (0.7828)T

L(1) = I = (0.7727) + (−0.3741)T
L(2) = J = (2.3307) + (0.1340)T
L(3) = K = (7.5082) + (0.9177)T

(β) Line defined by C(10) and C(14).

L(1) = I = (6.1647) + (0.3342)T
L(2) = J = (−0.2172) + (0.9171)T
L(3) = K = (−0.2670) + (−0.2175)T

L(1) = I = (1.7936) + (0.9726)T
L(2) = J = (2.3916) + (0.2177)T
L(3) = K = (6.7408) + (−0.0810)T

Crystal III

(a) Plane based on C(1), C(2), C(3), C(4) and C(5).

$$0.9391x + 0.2620y - 0.2224z = 2.5372$$

C(1)	0.0136	C(2)	−0.0071
C(3)	−0.0023	C(4)	0.0111
C(5)	−0.0153	Mo	−1.9982

(b) Plane based on C(14), C(15), C(16), C(17), C(18) and C(19).

$$0.5719x + 0.2861y + 0.7688z = 0.3403$$

C(14)	0.0072	C(15)	−0.0040
C(16)	−0.0001	C(17)	0.0010
C(18)	0.0024	C(19)	−0.0065

(c) Plane based on C(6), C(7), S(1) and N.

$$0.8877x + 0.3808y - 0.2588z = -0.2849$$

C(6)	−0.0016	C(7)	0.0016
S	0.0015	N	−0.0015
Mo	1.0329		

(d) Plane based on Mo, S, N and C(8).

$$0.5193x + 0.7446y - 0.4193z = 1.1208$$

Mo	−0.0025	S	0.0033
N	0.0052	C(8)	−0.0059
C(9)	−0.0242	C(10)	0.0058

(e) Plane based on N, C(10), C(11) and C(12).

$$-0.9075x + 0.3073y + 0.2865z = 2.7391$$

N	0.0458	C(10)	−0.0478
C(11)	−0.0416	C(12)	0.0436

(f) Equations of lines in orthogonal Å space
(α) Line defined by C(10) and C(11).

L(1) = I = (−1.9629) + (0.3224)T
L(2) = J = (2.3553) + (0.9466)T
L(3) = K = (0.6638) + (−0.0082)T

(β) Line defined by C(10) and C(14).

L(1) = I = (−1.1778) + (−0.7134)T
L(2) = J = (3.2484) + (−0.2238)T
L(3) = K = (0.1570) + (0.6641)T

TABLE 10 (continued)

Angles between planes

Plane 1	Plane 2	Angle		
		Crystal IIa		Crystal III
(a)	(d)	36.2	37.5	39.1
(b)	(d)	69.5	71.7	79.2
(e)	(d)	61.9	72.6	68.7
(a)	(b)	58.2	59.4	63.8

Angles between lines and planes

Line	Plane	Angle		
		Crystal IIa		Crystal III
(α)	(d)	32.8	27.1	28.9
(β)	(d)	32.7	40.2	35.3

TABLE 11

COMPARISON BETWEEN TORSIONAL ANGLES (°) [a] OF Ia, IIa AND III

Atoms				Angle			
A	B	C	D	Ia [b]	IIa		III
					Molecule I	Molecule II	
C(6)	Mo	S	C(8)	129.8	130.7	129.3	−129.0
C(6)	Mo	N	C(8)	−58.6	−64.4	−63.9	59.5
C(8)	N	C(10)	C(11)	130.9	117.5	107.7	−109.1
C(8)	N	C(10)	C(14)	−102.6	−113.8	−123.9	121.5
N	C(10)	C(14)	C(15)	−106.6	−89.6	−80.9	94.3
N	C(10)	C(14)	C(19)	73.2	91.1	97.2	−84.3

[a] According to the IUPAC—IUP convention [24], i.e. in the fragment ABCD, + = clockwise rotation of bond AB about bond BC so as to eclipse CD with AB along the line of sight (BC). [b] The numbering system used is consistent for crystals IIa and III but differs from that used for Ia, but the sequence is identical for all three compounds. For the inversion of the signs of the torsional angles, when compared with those given in ref. 5 see ref.25.

TABLE 12

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF THE DIASTEREOISOMER WITH A (—) ROTATION AT 578 nm

Refection number	Indices	F (calcd.) (hkl)	F (calcd.) $(\bar{h}\bar{k}\bar{l})$	Calcd. F [a] ratio	Meas. F [b] ratio
1	2, 2, $\bar{5}$	7.20	5.90	1.22	0.88
2	1, 1, $\bar{3}$	42.43	44.91	0.94	1.05
3	0, 2, $\bar{3}$	60.59	58.38	1.04	0.97
4	2, 4, $\bar{3}$	35.89	37.88	0.95	1.04
5	2, 2, $\bar{2}$	78.15	75.44	1.04	0.96
6	3, 1, $\bar{2}$	76.72	79.48	0.96	1.03
7	4, 1, $\bar{1}$	10.63	8.70	1.22	0.84
8	2, 3, $\bar{1}$	58.61	60.84	0.96	1.03
9	1, 5, $\bar{1}$	69.42	72.04	0.96	1.03

[a] Calcd. $F(hkl)$/calcd. $F(\bar{h}\bar{k}\bar{l})$. [b] Ratio of experimentally measured $F(hkl)/F(\bar{h}\bar{k}\bar{l})$.

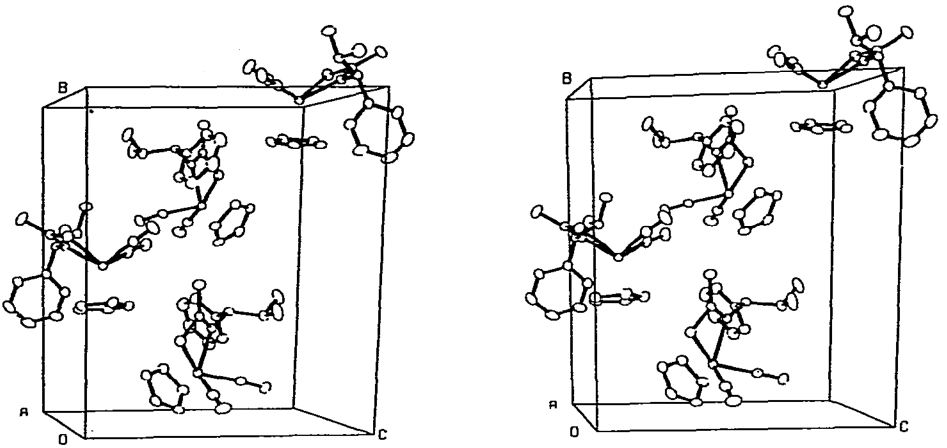


Fig. 3. A packing diagram of the molecules in their correct absolute configuration.

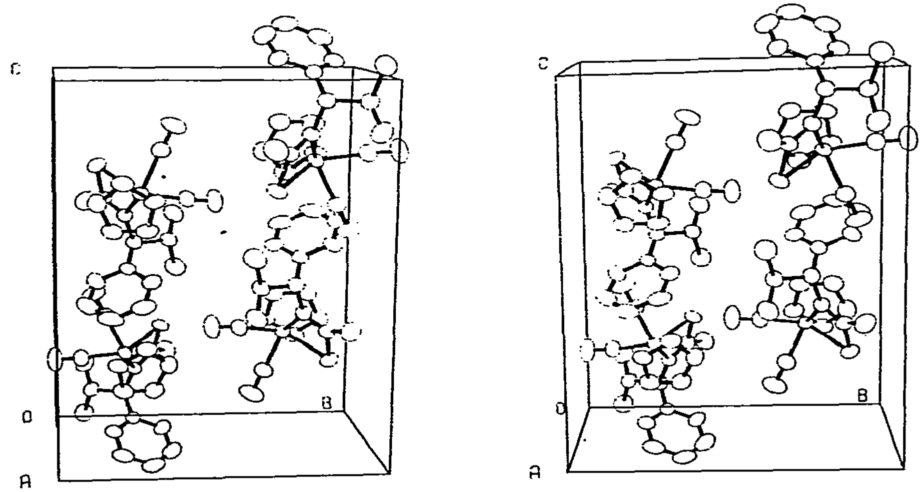


Fig. 4. A packing diagram of compound III.

Description of the molecular structure and discussion

As shown in Figs. 1—4, the molecules of IIa and III consist of a central Mo atom bound by a set of five ligands distributed in a distorted square-pyramidal arrangement. The thioamide ligand is bound to the Mo through the S and N atoms. This bidentate attachment of the thioamide ligand has only recently been documented structurally [5,18,19]. The distances and angles for the $(C_5H_5)Mo(CO)_2SCN$ fragment closely resemble those observed for compound Ia [5]. Table 13 was prepared in order to compare the geometry of the two independent molecules of the asymmetric unit of IIa and III with that of Ia. One notes that the Mo—S distances vary slightly (2.501(2) to 2.514(1) Å) while the Mo—N distances vary from 2.225(6) to 2.209(3) Å. Interestingly, as the length of the Mo—S bond increases, the Mo—N distances decrease. However,

TABLE 13

A COMPARISON OF STRUCTURAL PARAMETERS FOUND IN CpMo(CO)$_2$(thioacetamide) DERIVATIVI

Compound	Mo—S	Mo—N	Mo—C(O)	Mo—C(Cp) (average)	S—C	C—N	S—Mo—N
Ia	2.514(1)	2.209(3)	1.949(5) 1.966(5)	2.355	1.731(4)	1.306(5)	63.79(8)
IIa	2.5113(8)	2.220(2)	1.947(3) 1.957(3)	2.340	1.719(3)	1.303(3)	63.84(6)
	2.5072(9)	2.231(2)	1.953(3) 1.968(3)	2.348	1.718(3)	1.304(3)	63.77(6)
III	2.501(2)	2.225(6)	1.951(8) 1.966(8)	2.330	1.760(7)	1.281(10)	63.70(15)

[a] Bond lengths in Å, bond angles in degrees.

it is clear that none of the other molecular parameters changes very much for any of the four independent determinations. Thus, for the relationship of the structural parameters listed in Table 13 with other values in the literature, we refer the reader to our previous paper giving the crystal structure of compound Ia [5].

For the four different crystal structure determinations (all having R = CH$_3$) presented in Table 14, the angle between the planes of the (η^5-C$_5$H$_5$) and C$_6$H$_5$ rings is around 60°. However, we note that the angles observed for the optically active crystals are slightly smaller than those found for the racemic complexes which is, probably, a packing effect. All the compounds listed in Table 14 have the CH bond of the —CH(R′)(C$_6$H$_5$) group approximately in the plane of the chelate ring, the R′ substituent downward, whereas the phenyl group is oriented towards the (η^5-C$_5$H$_5$). This orientation of the phenyl group and the proton NMR spectra [7] suggest a weak interaction between the aryl and the (η^5-C$_5$H$_5$) groups, which persists even in solution [7]. Such an interaction offers a possible explanation for the greater induction caused by the asymmetric *CH(Aryl)(Alkyl) when compared to that of the *CH(Alkyl)(Alkyl′) [7]. The similarity in conformation of molecules Ia, of the two independent molecules of IIa and III can best be appreciated by referring to the values of the torsional angles given in Table 11. The small differences are impressive in view of the fact that there

TABLE 14

ANGLES BETWEEN THE (η^5-C$_5$H$_5$) AND C$_6$H$_5$ PLANES IN THE (η^5-C$_5$H$_5$)Mo(CO)$_2$SC(R)NR* COMPLEXES. R* = (S)-CHR′(C$_6$H$_5$)

Compound	R	R′	Space group	Angle between planes (°)	Reference
Ia	CH$_3$	CH$_3$	$P2_12_12_1$	61.3	5
IV	CH$_3$	CH$_2$CH$_3$	$P\bar{1}$	64.7	20
IIa	CH$_3$	CH(CH$_3$)$_2$	$P2_1$	58.2 59.4	This study
III	CH$_3$	CH(CH$_3$)$_2$	$P2_1/n$	63.8	This study

S—Mo—C(O) (*cis*)	S—Mo—C(O) (*trans*)	N—Mo—C(O) (*cis*)	N—Mo—C(O) (*trans*)	C(O)—Mo—C(O)	Ref.
78.5(2)	122.8(2)	88.5(2)	118.4(2)	72.8(2)	5
81.63(9)	126.1(1)	88.9(1)	119.7(1)	72.8(1)	This study
80.74(9)	125.6(1)	86.7(1)	118.3(1)	74.6(1)	This study
79.8(3)	123.6(3)	87.1(3)	118.8(3)	73.9(3)	This study

are large, flexible fragments which are connected by single bonds. More explicitly, the phenyl ring of the optically active carbons could readily move out of the region of the Cp ring by a variety of simple changes of the torsional angles, all of which are found, by the use of scaled models, to be quite reasonable and free of major steric hindrance. Thus, the effect of packing on the geometry and conformation of these substances seems to be marginal and the stability of a preferred conformation (even in solution; vide supra) is in sharp contrast with well-documented cases in which the two crystallographically independent enantiomers of a given asymmetric unit acquire drastically different conformations (i.e., see the cases of valine and iso-leucine [21] where these differences are very large).

Crystal packing of the active and racemic compounds

Comparisons of the structures of some enantiomers with those of their corresponding racemates reveal, in a number of cases [22], packing features common to the two structures which are either one or two dimensional and in the form of either columns or layers of molecules with the same stereochemical configuration. The packing mode of the racemic compound III can be described as columns of adjacent molecules having opposite absolute configurations. These

TABLE 15

INTERMOLECULAR DISTANCES (NEAREST NEIGHBORS) FOR COMPOUND IIa (Å) [a]

$O(2)^{II}—H(133)^{III}$	2.81
$C(11)^{II}—H(133)^{III}$	3.20
$C(13)^{II}—H(3)^{IV}$	3.05
$C(13)^{I}—H(11)^{IV}$	3.33
$O(1)^{II}—H(132)^{IV}$	3.35

[a] Symmetry codes:

I	(x, y, z)	First molecule
II	(x, y, z)	Second molecule
III	$(-x, \frac{1}{2} + y, -z)$	First molecule
IV	$(-x, \frac{1}{2} + y, -z)$	Second molecule.

TABLE 16

INTRAMOLECULAR AND INTERMOLECULAR DISTANCES (NEAREST NEIGHBORS) FOR COMPOUND III (Å) [a]

C(14)^{I}—C(4)^{I}	3.47
C(19)^{I}—C(4)^{I}	3.46
C(19)^{I}—C(5)^{I}	3.33
C(13)—H(2)^{II}	2.94
C(14)—H(2)^{II}	3.09
C(18)—H(2)^{II}	3.22
C(19)—H(2)^{II}	2.98
C(2)—H(132)^{II}	3.16

[a] Symmetry codes:
I (x, y, z)
II $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

columns, along the [001] direction, are characterized by alternating phenyl and C_5H_5 groups. Thus, the two closest neighbors of the C_5H_5 group are two phenyl rings, one intramolecular, the other intermolecular (see Table 16). The two phenyl rings are approximately parallel, the C_5H_5 group being sandwiched between them (see Fig. 4). In the case of the active IIa compound, the closest intermolecular distances are no longer between the phenyl and C_5H_5 rings (see Table 15). The packing can again be described as columns of alternating C_5H_5 and phenyl groups. The columns are along the [001] and [100] directions. However, in this case the two phenyl rings are far from being parallel (see Fig. 3). Thus, the packing of the active and racemic compounds differ considerably. As previously stated, the angle between the planes of the phenyl and C_5H_5 rings of the same molecule does not change significantly (Table 14). Thus, the special relationship between these two groups cannot be a result of packing and, in fact, it remains unchanged even in solution as proven by their proton NMR spectra [7]. Kuroda and Mason [22] determined the crystal structure and absolute configuration of (—)-tris(pentane-2,4-dionato)chromium(III) and compared its packing with that of the racemic pair [23]. It was found that the latter has a more compact structure, which is reflected in the observed densities (1.28 and 1.36 g cm^{-3} for the active and racemic crystals, respectively). In our case, densities of the two compounds are almost identical despite the difference in packing contacts and the difference in the space groups in which they crystallize.

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