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The Absolute Configurations of Organometallic Compounds. XX. The Conformations and Absolute Configurations of Four Preferred and Non-Preferred Diastereoisomers having Composition $(R''\text{-}C_5H_4)Mo(CO)_2[(HCPhR)\text{–}N(C\text{–}Ph)\text{–}N\text{–}(HCPhR')]$

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The structures and absolute configurations of four optically resolved compounds having composition $(R''\text{-}C_5H_4)Mo(CO)_2[(HCPhR)-N(CPh)-N-(HCPhR')]$ *were established by X-ray diffraction methods. Benz I* [$R'' = R' = H$, $R = \text{-}CH_3$]: *triclinic, space group P1;* $a = 9.792(3)$, $b = 11.875(4)$, $c = 11.885(3)$ Å, $\alpha = 88.27(2)$, $\beta = 67.42(2)$ *and* $\gamma = 83.71°$. *Cell volume* = 1268.21 Å^3, $Z = 2$ *molecules/unit cell. Benz II* [$R'' = R' = H$, $R = \text{-}CH_3$]: *orthorhombic, space group* $P2_12_12_1$; $a = 9.885(3)$, $b = 11.550(5)$, $c = 22.620(9)$ Å. *Cell volume* = 2623.67 Å^3, $Z = 4$ *molecules/unit cell. Benz I and II are of identical composition and differ only in conformation at the* $(\text{-}CH(CH_3)Ph)$ *substituent of the benzamidine ligand, the former being the thermodynamically preferred stereoisomer.*

Benz III differs from Benz I and Benz II in that both nitrogens of the benzamidine ligand bear optically active substituents of composition $(\text{-}CH(CH_3)\text{-}Ph)$; *therefore* $R'' = H$ *and* $R' = R = \text{-}CH_3$. *The substance crystallizes in the space group* $P2_12_12_1$ *with* $a = 9.656(2)$, $b = 11.691(7)$ *and* $c = 23.562(6)$ Å. *Cell volume* = 2660.08 Å^3 *and* $Z = 4$ *molecules/unit cell. Like Benz II, this is also a non-preferred stereoisomer.*

Finally, Benz IV, like Benz III, has optically active substituents at both benzamidine ligand nitrogens, but also bears a methyl substituent at Cp; i.e., $R'' = R' = R = CH_3$. *Orthorhombic,* $P2_12_12_1$; $a = 9.737(7)$, $b = 11.716(4)$ *and* $c = 23.661(9)$ Å. *Cell volume* = 2698.96 Å^3, $Z = 4$ *molecules/unit cell. This is also a non-preferred stereoisomer.*

For the convenience of the reader, all of this terminology is reviewed in the Introduction.

The two independent molecules in the asymmetric unit of Benz I (Benz Ia and Benz Ib) have essentially identical bond lengths and angles and slightly different inter-planar angles associated with the phenyl rings, which have large areas over which packing forces can exert substantial torsional pressures. Benz II, III and IV also have few differences among themselves or with Benz Ia and Benz Ib insofar as bond lengths and angles are concerned, but differ somewhat in their interplanar angles in the same manner described for Benz I.

Details of conformational and configurational problems in this series are given in the text.

Introduction

During the past six years we have published a series of studies concerned with the structures, conformations and absolute configurations of organometallics [1–16] comprising a wide variety of metals, ligands and coordination types. Among them were a series of diastereoisomers containing bidentate Schiff bases derived from either pyridine carbaldehyde or pyrrole carbaldehyde and the optically active amines $H_2N\text{–}CRHPh$ (R = Me, Et, i-Pr, *etc.* ...) either in the (*S*) or (*R*) absolute configuration at the optically active carbon atom [1, 3, 12]. A large number of examples of diastereoisomers having composition $(h^5\text{-}C_5H_5)Mo(CO)_2$(Optically Active Thioamide) have been studied and reported already from our group [3, 11, 13]. In this paper, we address ourselves to the stereochemical problems associated with the conformations and absolute configurations of a new class of compounds, namely the benzamidines shown schematically in Fig. 1.

Hereafter, for the sake of compactness and convenience, we will refer to the four species described in this report by the following abbreviations:

Benz I ... $R'' = R' = H$; $R = \text{-}CH_3$ See Fig. 1
This is a preferred diastereoisomer

Benz II ... $R'' = R' = H$; $R = \text{-}CH_3$ See Fig. 1
This is a non-preferred diastereoisomer

Benz III ... $R'' = H$; $R' = R = \text{-}CH_3$ See Fig. 1
This is a non-preferred diastereoisomer

Benz IV ... $R'' = R' = R = \text{-}CH_3$ See Fig. 1
This is a non-preferred diastereoisomer also

In our previous papers [1–16], we have defined a preferred diastereoisomer (P) as that which is predominant at equilibrium in solution at a given temperature, which for these systems is very frequently around 70 °C. A very thorough description of the nature of these equilibria, their half-life values, *etc.*,

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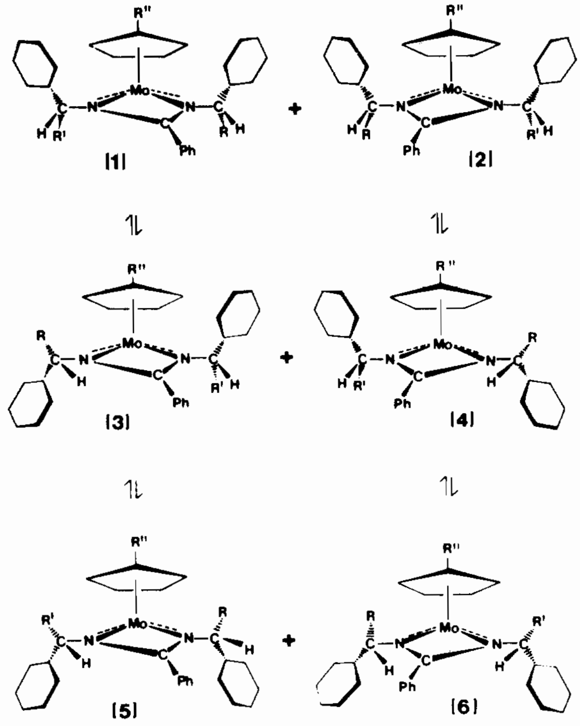

Fig. 1. Possible stereoisomers in Mo–benzamidine series.

has been given by Henri Brunner in his most recent review [17]. We have published the structural and crystallographic fundamentals in the preceding sixteen papers. In order to avoid lengthy and undue repetition, the interested reader is referred to those sources [1–17].

Briefly, we found earlier [1, 3, 11–13] for the case of square-pyramidal coordination (the current case) compounds having the general composition

$$(h^5\text{-}C_5H_5)Mo(CO)_2(L_1L_2)$$

that if the bidentate ligand, L_1L_2, has a side chain in which a phenyl ring is located at the position *beta* (β) with respect to the central atom (Mo), the phenyl ring acquires either of two orientations with respect to the Cp ring: (a) directly in front of it in such orientation that the edge of Cp faces the plane of the phenyl and points nearly at its center, or (b) directly away from it and nearly 180° from the position it occupies in case (a). Invariably, the preferred diastereoisomer has been shown in at least 50 cases (see refs. 10 and 17 and references therein) to have the phenyl oriented in the manner described in (a) and as shown in a number of examples in Fig. 1. However, thus far the compounds studied in the thioamide and Schiff base series contained only one phenyl ring capable of such Cp–Ph interactions. The substances we are dealing with now, the benzamidines shown schematically in Fig. 1, were designed to be capable of two such contacts if this seemed energetically desirable. All of this work has been done in collaboration with Professor Henri Brunner.

In two recent, brief notes [9, 10], we announced the successful syntheses and resolutions of Benz I and Benz II and gave preliminary information concerning the diastereoisomeric ratios in solutions of acetone at 70 °C, *etc.* The details of such solution physical data will be published separately by Brunner and Agrifoglio [18] and constitutes part of the doctoral thesis of Agrifoglio [19]. In this paper, we will concentrate almost exclusively on the crystal structure determinations and on the conformational and configurational information that can be extracted from them.

Experimental

Data Collection and Processing

All data sets were collected by the same procedure using a computer-controlled Enraf-Nonius CAD-4 diffractometer operating under the OS/4 software package [20]. All crystals were mounted on XYZ-translational heads and 25 reflections were searched for and were automatically centered. After orientation and a Niggli [21] matrix were computed, Roof's tables [22] were used to determine the crystal system and the space group symbol. Absences were searched for by judicious scans of appropriate reflections. A suitable set of 25 high angle reflections were found which were both strong and properly spread over reciprocal space and carefully centered to define accurate lattice constants. After that, data were collected according to the nature of the problem at hand. Details of those parameters used for data collection or data processing are given on Tables I–IV, respectively, for Benz I–Benz IV. Important crystallographic parameters derived from data processing are also listed in those tables. A few other general remarks may be useful:

(a) Mo-Kα radiation was used throughout since it reduces absorption problems to a negligible nuisance level. Radiation was monochromatized with a dense graphite crystal assumed, for all practical purposes, to be ideally imperfect. The polarization correction used was that given by Kerr and Ashmore [23].

(b) Data decoding and reduction were carried out with a local program written by J. D. Korp [24].

(c) A decay correction was needed in one case (Benz II). An analysis of the decay curves, based on our standard reflections, was carried out *via* the program SYSTD written by Hseu and modified by Korp [25].

(d) All crystallographic data processing beyond data reduction was carried out with SHELX-76 [26], using the scattering curves listed in reference 27. Distances between non-bonded atoms were computed

TABLE I. Crystallographically Important Data Collection and Data Processing Information for Benz-I.

Empirical formula	$C_{29}H_{26}N_2O_2Mo$
Molecular weight	530.48 g mol^{-1}
Cell constants	$a = 9.792(3)$ Å
	$b = 11.875(4)$ Å
	$c = 11.885(3)$ Å
	$\alpha = 88.27(2)^\circ$
	$\beta = 67.42(2)^\circ$
	$\gamma = 83.71(2)^\circ$
Unit cell volume	1268.21 Å^3
Space group	P1
Density: measured	1.40 g cm^{-1}
calculated (Z = 2)	1.389 g cm^{-1}
Absorption coefficient (MoK_α)	4.74 cm^{-1}
Radiation used for data collection	MoK_α ($\lambda = 0.71069$ Å)
Scanning range for 2θ	$4.0 \leqslant 2\theta \leqslant 50.0^\circ$
Crystal approximately along	[1, 1, 0]
Standards for intensity control (measured every 2 hr exposure time)	$[\bar{4}, 4, \bar{2}]$ and $[\bar{4}, 5, 0]$
Scan width for each reflection	$\Delta\theta = (1.00 + 0.35 \tan\theta)$
Maximum scan time	300 sec.
Prescan acceptance criterion[a]	$I_{pre} \geqslant 1.9\sigma(I_{pre})$
Scan technique	θ:2θ
Total number of reflections collected[b]	3911
Number of contributing reflections in the last cycle of least-squares	3572
Number of variables	388
Weighting scheme	unit weights
Largest parameter shift in the last cycle of least-squares	0.02·ESD
Largest peak in final difference Fourier	0.58 e Å^{-3}
Final R(F)[c]	0.0377
Final R_w(F)[d]	0.0382

[a] In the new CAD-4 software, the above criterion is used instead of a minimum number of counts on prescan. [b] Out of 3911 reflections, 3584 with $I \geqslant 2\sigma(I)$ were classified as 'observed'; the remaining 351 were termed 'less than' and were not used after data reduction. An additional 12 low angle reflections were omitted from the latter refinement stages due to apparent secondary extinction effects. [c] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE II. Crystallographically Important Data Collection and Data Processing Information for Benz-III.

Empirical formula	$C_{30}H_{28}N_2O_2Mo$
Molecular weight	544.50 g mol^{-1}
Cell constants	$a = 9.656(2)$ Å
	$b = 11.691(7)$ Å
	$c = 23.562(6)$ Å
Unit cell volume	2660.08 Å^3
Space group	$P2_12_12_1$
Density: measured	1.36 g cm^{-1}
calculated (Z = 4)	1.359 g cm^{-1}
Absorption coefficient (MoK_α)	4.53 cm^{-1}
Radiation used for data collection	MoK_α ($\lambda = 0.71069$ Å)
Scanning range for 2θ	$4.0 \leqslant 2\theta \leqslant 60^\circ$
Crystal approximately along	[100]
Standards for intensity control (measured every 2 h exposure time)	$[\bar{4}, \bar{2}, 5]$ and $[2, 2, 6]$
Scan width for each reflection	$\Delta\theta = (0.95 + 0.35 \tan\theta)^\circ$
Maximum scan time	120 sec.
Prescan acceptance criterion[a]	$I_{pre} \geqslant 1.9\sigma(I_{pre})$
Scan technique	θ:2θ
Total number of reflections collected[b]	4398
Number of contributing reflections in the last cycle of least-squares	2189
Number of variables	201
Weighting scheme	unit weights
Largest parameter shift in the last cycle of least-squares[c]	0.75 [0.05] ·ESD
Largest peak in final difference Fourier	0.66 e Å^{-3}
Final R(F)[d]	0.0471
Final R_w(F)[e]	0.0483

[a] In the new CAD-4 software, the above criterion is used instead of a minimum number of counts on prescan. [b] Out of 4398 reflections collected, 2205 with $I \geqslant 2\sigma(I)$ were classified as 'observed'; the remaining 2193 were termed 'less than' and were not used after data reduction. An additional 16 low angle reflections were omitted from the latter refinement cycles due to apparent secondary extinction effects. [c] Positional and rotational parameters for the rigid-body Cp groups were strongly correlated, yielding relatively large parameter shifts throughout the refinement. All other parameters did converge giving final parameter shifts with absolute values of less than 0.05 times their respective ESD's. [d] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [e] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

with ORFFE [28], positions of idealized hydrogens either with SHELX-76 or with HIDEAL [29]. Torsional angles were computed with TORSION [30], which employs the conventions of the IUPAC-IUB Commission on Biological Nomenclature [31].

(e) Absolute configurations were determined by measuring a number of Bijvoet [32] pairs for which the differences were larger than $3\sigma(I)_{meas}$. Usually the differences were much larger than that. Details are listed in Tables V–VII.

(f) Structures were solved either by examination of the Patterson function or *via* MULTAN [33].

(g) Stereo plots of the molecules and packing diagrams were generated with ORTEP-2 [34] and double stereo plots used to compare molecular conformations of related pairs were generated with BMFIT [35].

(h) Details of the decay correction are given in M. W. Creswick's thesis [36]. Briefly, two reflections $[\bar{5}, \bar{2}, 1$ and $0, \bar{1}, 14]$ were used as intensity standards. These were observed to decay in intensity over the period of data collection. Fig. 2 is a plot of

TABLE III. Crystallographically Important Data Collection and Data Processing Information for Benz II.

Empirical formula	$C_{29}H_{26}N_2O_2Mo$
Molecular weight	530.48 g mol^{-1}
Cell constants	a = 9.885(3) Å b = 11.550(5) Å c = 22.620(9) Å
Unit cell volume	2623.67 Å^3
Space group	$P2_12_12_1$
Density: measured	1.41 g cm^{-1}
calculated (Z = 4)	1.343 g cm^{-1}
Absorption coefficient (MoK_α)	4.58 cm^{-1}
Radiation used for data collection	MoK_α (λ = 0.71069 Å)
Scanning range for 2θ	$4.0 \leqslant 2\theta \leqslant 65.0°$
Crystal approximately along	[100]
Standards for intensity control (measured every 2 hr exposure time)	$[0, \bar{1}, 14]$ and $[\bar{5}, \bar{2}, 1]$
Scan width for each reflection	$\Delta\theta = (0.95 + 0.35 \tan\theta)°$
Maximum scan time	180 sec.
Prescan acceptance criterion[a]	$I_{pre} \geqslant 1.9\sigma(I_{pre})$
Scan technique	θ:2θ
Total number of reflections collected[b]	3834
Number of contributing reflections in the last cycle of least-squares	1898
Number of variables	191
Weighting scheme	unit weights
Largest parameter shift in the last cycle of least-squares	0.05•ESD
Largest peak in final difference Fourier	0.48 e Å^{-3}
Final R(F)[c]	0.0413
Final R_w(F)[d]	0.0415

[a] In the new CAD-4 software, the above criterion is used instead of a minimum number of counts on prescan. [b] Out of 3834 reflections collected, 1914 with $I \geqslant 2\sigma(I)$ were classified as 'observed'; the remaining 1920 were classified as 'less than' and were not used after data reduction. An additional 16 low angle reflections were omitted from the latter refinement stages due to apparent secondary extinction effects. [c] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE IV. Crystallographically Important Data Collection and Data Processing Information for Benz-IV.

Empirical formula	$C_{31}H_{30}N_2O_2Mo$
Molecular weight	557.52 g mol^{-1}
Cell constants	a = 9.737(7) Å b = 11.716(4) Å c = 23.661(9) Å
Unit cell volume	2698.96 Å^3
Space group	$P2_12_12_1$
Density: measured	1.36 g cm^{-1}
calculated (Z = 4)	1.372 g cm^{-1}
Absorption coefficient (MoK_α)	4.47 cm^{-1}
Radiation used for data collection	MoK_α (λ = 0.71069 Å)
Scanning range for 2θ	$4.0 \leqslant 2\theta \leqslant 64°$
Crystal approximately along	[100]
Standards for intensity control (measured every 2 hr exposure time)	$[\bar{2}, 0, \bar{6}]$ and [3, 1, 7]
Scan width for each reflection	$\Delta\theta = (1.0 + 0.35 \tan\theta)°$
Maximum scan time	240 sec.
Prescan acceptance criterion[a]	$I_{pre} \geqslant 1.9\sigma(I_{pre})$
Scan technique	θ:2θ
Total number of reflections collected[b]	4417
Number of contributing reflections in the last cycle of least-squares	2541
Number of variables	175
Weighting scheme	$w = [\sigma(F_o)]^{-2}$
Largest peak in final difference	0.52 e Å^{-3}
Final R(F)[c]	0.0475
Final R_w(F)[d]	0.0414

[a] In the new CAD-4 software, the above criterion is used instead of a minimum number of counts on prescan. [b] Out of 4417 reflections collected, 2541 unique with $I > 3\sigma(I)$ were classified as 'observed'; the remaining 2193 were standards, redundant or 'unobserved' and were not used after data reduction. An additional 16 low angle reflections were omitted from the later refinement cycles due to apparent secondary extinction effects. [c] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [d] $R_w(F) = [\Sigma w(|F_o - F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

the rate of decay of both, which is seen to be nearly identical and to fit the linear equation

$$y = a + bx$$

with a = 1.00 and b = –0.000979. The entire data set was corrected for decay and the improvement in the least-squares refinement and on the quality of the derived stereochemical parameters was marked.

(i) One final comment concerning the refinement of the Cp rings in the cases of Benz II and Benz III: in both these substances the Cp ring occupies two crystallographic positions as became clear from difference maps based on ring occupancy of 100% at a single position. Two Cp images were located at the sites indicated by the electron density maps and their occupancy numbers refined. As a result, not only did the refinement improve but the occupancy numbers have very sensible magnitudes. The interested reader is referred to Creswick's thesis [36] where this subject is dealt with at length.

Results and Discussion

In what follows, the Discussion will be divided into two parts associated with the fact that Benz I and Benz II are, respectively, the preferred and the non-preferred diastereoisomers of the substance with $R'' = R' = H$, $R = \text{-}CH_3$ and the optically active carbon (C22) is (*S*), whereas Benz III and Benz IV contain two optically active carbon (C15 and C22) and both are non-preferred diastereoisomers different only by the fact that, in Benz IV, the Cp ring is methylated. The object of methylating the Cp ring

TABLE V. Bijvoet Pairs for Benz-I.

	Calculated			Observed				
hkl	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	Ratio[a]	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	N	$\sigma(F)_{av}$	Ratio[b]
$\bar{2}\bar{1}1$	40.65	42.23	0.96	38.87	41.52	8	0.23	0.94
230	24.24	22.48	1.08	23.56	21.42	8	0.26	1.10
$\bar{5}10$	24.51	25.34	0.97	22.21	23.47	8	0.36	0.95
$\bar{1}40$	31.49	30.87	1.02	29.64	28.40	8	0.27	1.04
301	29.16	28.59	1.04	26.93	25.73	8	0.25	1.05
$\bar{2}21$	33.37	33.91	0.95	31.23	32.63	8	0.26	0.96
$\bar{1}\bar{2}1$	27.41	26.36	1.08	30.84	28.91	4	0.21	1.07
$\bar{1}32$	44.76	45.36	0.98	49.02	51.11	4	0.26	0.96
$\bar{1}\bar{2}3$	18.74	18.54	1.06	21.42	20.08	4	0.28	1.07

[a] $F(hkl)_{calc}/F(\bar{h}\bar{k}\bar{l})_{calc}$. [b] $F(hkl)_{avg}/F(\bar{h}\bar{k}\bar{l})_{avg}$, with each F_{avg} determined from N replicate intensity measurements.

TABLE VI. Bijvoet Pairs for Benz-II.

	Calculated			Observed				
hkl	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	Ratio[a]	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	N	$\sigma(F)_{av}$	Ratio[b]
116	37.17	39.03	0.95	32.70	34.46	8	0.24	0.95
326	36.74	37.42	0.98	30.23	30.95	4	0.30	0.98
124	88.04	90.41	0.97	75.51	77.58	5	1.04	0.97

[a] $F(hkl)_{calc}/F(\bar{h}\bar{k}\bar{l})_{calc}$. [b] $F(hkl)_{avg}/F(\bar{h}\bar{k}\bar{l})_{avg}$, with each F_{avg} determined from N replicate intensity measurements.

TABLE VII. Bijvoet Pairs for Benz-III.

	Calculated			Observed				
hkl	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	Ratio[a]	F(hkl)	F($\bar{h}\bar{k}\bar{l}$)	N	$\sigma(F)_{av}$	Ratio[b]
131	29.53	28.39	1.04	27.37	26.10	5	0.23	1.05
152	32.35	33.29	0.97	28.76	29.88	5	0.30	0.96
115	13.23	12.16	1.09	13.14	12.02	5	0.24	1.09
126	14.29	13.11	1.09	13.31	12.19	5	0.27	1.09
137	37.45	38.21	0.98	33.94	34.72	5	0.29	0.98
117	53.77	55.38	0.97	50.98	52.42	5	0.25	0.97
133	12.13	12.65	0.96	11.31	11.92	4	0.27	0.95

[a] $F(hkl)_{calc}/F(\bar{h}\bar{k}\bar{l})_{calc}$. [b] $F(hkl)_{avg}/F(\bar{h}\bar{k}\bar{l})_{avg}$, with each F_{avg} determined from N replicate intensity measurements.

was suggested by the observation that, in solution, the Cp ring is freely rotating when it is unsubstituted. We wanted to probe the effect, if any, of methylating the ring upon the equilibria between preferred and non-preferred diastereoisomers and what stereochemical effect such a substitution would cause.

Benz I and Benz II

Common structural features

The compounds Benz I and Benz II (Fig. 3–12) represent the first pair of pure, isolated, organometallic diastereoisomers to be structurally characterized and compared directly. Table XII lists structural parameters for the two independent molecules (A and B) of Benz I as compared to the single molecule of Benz II. Both compounds consist of square-pyramidal $Cp(CO)_2MoNCN$ fragments, having almost planar Mo–N–C–N chelate rings (Tables XV and XVI). Most bonding parameters within the $Cp(CO)_2$-MoNCN fragments agree from one compound to the next. Within the peripheral Ph, CH_2Ph and CHMePh groups, all phenyl rings are strictly planar (Table XV and XVI). Minor variations in distances and angles within the rings may be attributed to the relatively low ratio of observed data/variable parameters since Benz I has a large number of independent atoms (two molecules in the asymmetric unit).

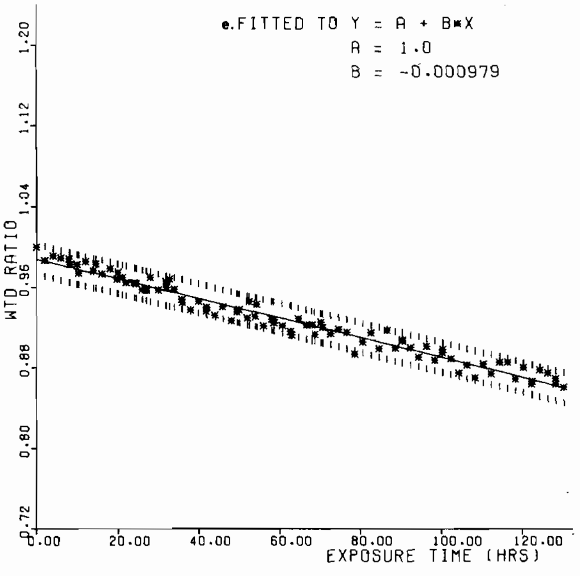

Fig. 2. Least-squares fit of intensity standards for Benz II [$\bar{5}$, $\bar{2}$, 1 and 0, $\bar{1}$, 14] as a function of X-ray exposure time. The data were fitted with program SYSTD [25] and the dashed lines above and below the fitted curve enclose a 2σ(I) probability region.

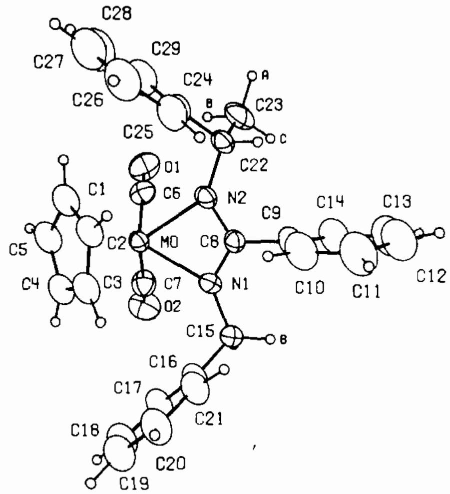

Fig. 3. Single view of Benz Ia showing absolute configuration and atom labeling scheme. (This figure and all other single views, stereo views and packing diagrams were calculated using ORTEP-2 [34]. Heavy atoms are represented by 50% probability ellipsoids, while hydrogens are depicted as spheres of arbitrary size.)

In each complex, he exocyclic phenyl group [C(9)–C(14)] is almost perpendicular to the Mo–N(1)–C(8)–N(2) (ligand) plane; the interplanar angles in Benz IA, Benz IB and Benz II are: 89.23, 87.84 and 75.28°, respectively. The three C(8)–C(9) distances are equal to within 3σ (see Table XXXII) and are slightly larger than the 1.477 Å expected [37] for a carbon–carbon sp^2–sp^2 single bond. As in the case of one of our thioamides [13] (which has an exocyclic α-naphthyl group), there is little or no conjugation between the two aromatic fragments. This lack of conjugation was also noted by Cotton *et al.* [38a, b] in two benzamidine complexes in which N(Ph)C(Ph)N(Ph) was used as an *N,N'*-bridging ligand.

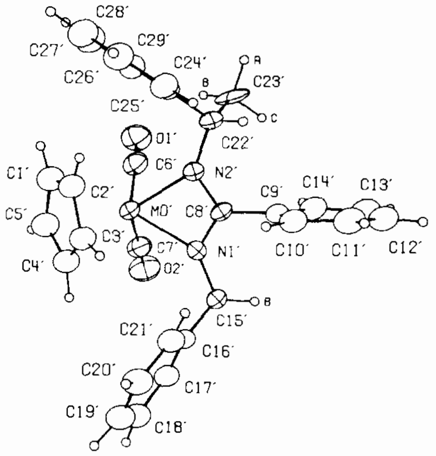

Fig. 4. Absolute configurations of Benz Ib.

Additional structural features in Benz I

Molecular geometries for the two independent molecules of Benz I are shown in Fig. 3–6 and the packing of the molecules in the unit cell in Fig. 11. According to the nomenclature rules suggested previously [6, 7, 17], the priority sequence (η^5-Cp) > N(CHMePh) > N(CH_2Ph) > C(O) may be used to assign the chirality indicator (*R*) at each of the Mo sites. Thus, a chirality of (*S*) at the optically active carbon (situated β to Mo) induces a chirality of (*R*) at the Mo site in this preferred (P) diastereoisomer.

Comparison of Benz IA and IB Figure 9 provides a visual comparison of conformation differences between the two independent molecules of Benz I. In both molecules, the two N-substituent fragments are oriented with their phenyl rings facing the apical Cp group. Between the optically active side groups, only minor deviations can be seen in the relative positions of corresponding carbon atoms. Between the two CH_2Ph groups, however, there are greater differences in the location of corresponding phenyl rings. Although hydrogen atoms are not included in Fig. 9, the torsion angles listed in Table XII show that for both side groups (in both molecules), hydrogens can be found close to the Mo–N–C–N (ligand) plane.

The major conformational difference between molecules A and B of Benz I occurs in the orientation of the two Cp groups with respect to other ligands in the square-pyramid. For molecule A, the minimum torsion angle (see Table XII) between Cp carbons and

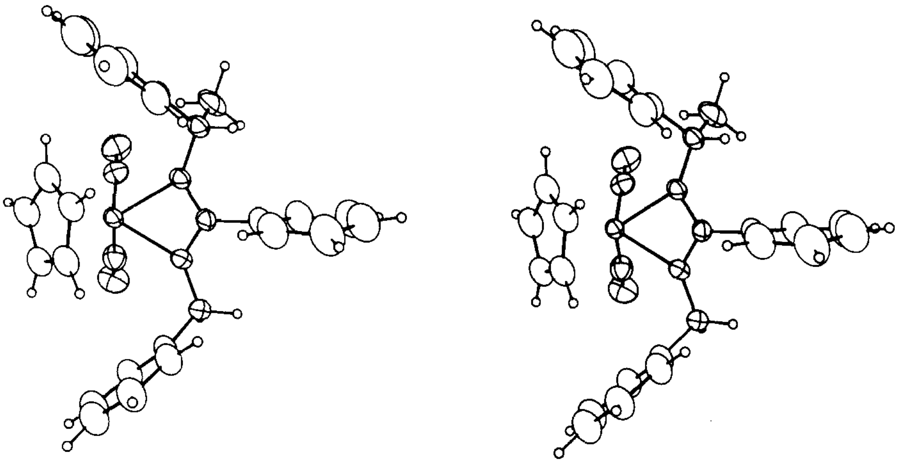

Fig. 5. Stereo view of Benz Ia.

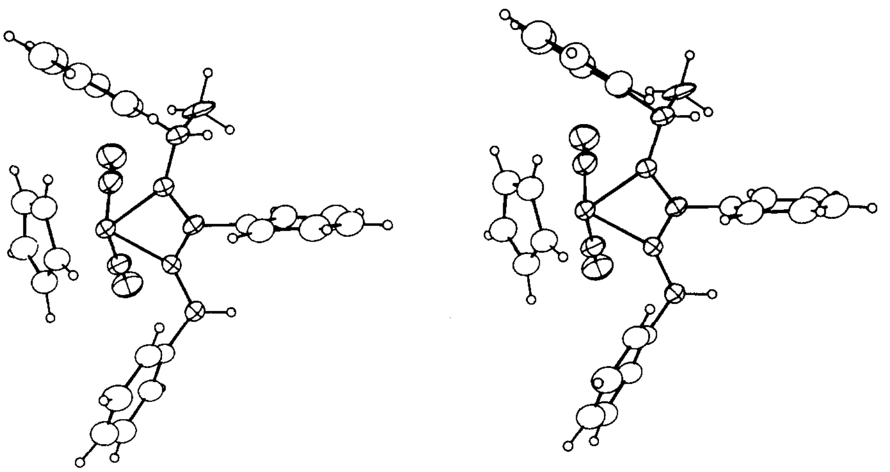

Fig. 6. Stereo view of Benz Ib.

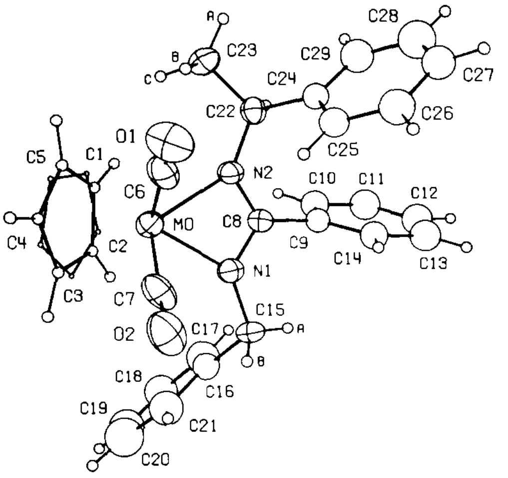

Fig. 7. Absolute configuration of Benz II.

the four basal ligand-atoms [*i.e.*, C(Cp)–Cp(centroid)–Mo–N(or C)] occurs between C(1) and N(1). In molecule B a similarly constructed minimum torsional angle relates atoms C(3) and N(2). In both cases, a carbon atom in the apical Cp ring eclipses a nitrogen in the base of the square-pyramid.

Additional structural features in Benz II

The molecular geometry of Benz II is depicted in Fig. 7 and 8. According to the nomenclature rules suggested previously [6, 7, 17], the chirality at the Mo site in this non-preferred (NP) diastereomer may be designated as (*S*). Thus, the chirality of the molecule may be written as (*S*;C)(*S*;Mo).

The disordered Cp group One additional structural feature in Benz II, as compared to Benz I (A or B) results from refinement of the Cp group as two images [36]. In Figures 7 and 8, the major (70%) Cp image is depicted with hydrogen atoms attached, while the minor (30%) image is shown without hydrogens. Torsional angles (Table XII) show that for the major (70%) image, one Cp carbon, C(1), eclipses one nitrogen atom, N(2), at the base of the square-

TABLE VIII. Coordinates and Thermal Parameters ($\times 10^3$, Mo $\times 10^4$, H $\times 10^2$).

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MO	0.47850(0)	0.47850(0)	0.47850(0)	579(5)	430(4)	525(6)	−32(4)	−248(4)	20(4)
O1	0.8151(8)	0.3923(7)	0.3666(7)	60(4)	138(7)	104(6)	4(4)	−23(4)	−23(5)
O2	0.5723(10)	0.5093(8)	0.1999(8)	122(7)	126(7)	54(5)	−7(5)	−27(5)	12(4)
N1	0.3203(8)	0.3721(5)	0.4611(7)	74(5)	51(4)	82(5)	−3(3)	−47(4)	7(4)
N2	0.4429(8)	0.3160(5)	0.5736(7)	78(5)	42(3)	63(5)	−10(3)	−37(4)	11(3)
C1	0.4914(10)	0.5924(7)	0.6279(9)	68(2)					
C2	0.3417(9)	0.5723(7)	0.6705(8)	63(2)					
C3	0.2817(10)	0.6214(7)	0.5864(8)	67(2)					
C4	0.3943(10)	0.6705(7)	0.4937(9)	66(2)					
C5	0.5220(12)	0.6564(9)	0.5203(10)	72(3)					
C6	0.6892(10)	0.4230(8)	0.4099(9)	64(6)	86(6)	72(7)	−6(5)	−29(5)	−4(5)
C7	0.5364(14)	0.4953(10)	0.3025(13)	91(8)	77(7)	73(9)	1(6)	−29(7)	−14(6)
C8	0.3405(10)	0.2956(7)	0.5354(9)	63(5)	46(4)	53(6)	−2(4)	−25(5)	−4(4)
C9	0.2541(9)	0.1928(7)	0.5726(8)	62(2)					
C10	0.1221(12)	0.1992(10)	0.6728(11)	93(3)					
C11	0.0369(15)	0.1057(12)	0.7073(13)	119(4)					
C12	0.1058(16)	0.0047(12)	0.6419(14)	110(4)					
C13	0.2191(15)	−0.0035(11)	0.5450(12)	113(4)					
C14	0.3033(12)	0.0927(9)	0.5055(10)	87(3)					
C15	0.2240(10)	0.3714(7)	0.3952(9)	77(6)	57(5)	79(7)	0(4)	−46(5)	−1(4)
C16	0.1193(9)	0.4803(7)	0.4202(8)	59(2)					
C17	0.1513(10)	0.5691(7)	0.3407(8)	70(2)					
C18	0.0627(11)	0.6710(9)	0.3681(10)	85(3)					
C19	−0.0622(11)	0.6839(9)	0.4775(10)	85(3)					
C20	−0.0936(11)	0.5965(9)	0.5563(10)	84(3)					
C21	−0.0055(10)	0.4940(8)	0.5283(9)	71(2)					
C22	0.4969(9)	0.2436(6)	0.6517(8)	74(5)	45(4)	70(6)	−5(4)	−34(5)	11(4)
C23	0.6446(14)	0.1748(9)	0.5744(11)	131(10)	84(7)	101(9)	43(7)	−54(8)	−9(6)
C24	0.5071(9)	0.3134(7)	0.7522(8)	57(2)					
C25	0.3818(10)	0.3400(8)	0.8546(9)	75(2)					
C26	0.3954(14)	0.4114(10)	0.9468(11)	101(3)					
C27	0.5338(15)	0.4436(11)	0.9236(13)	100(4)					
C28	0.6426(15)	0.4220(11)	0.8317(13)	114(4)					
C29	0.6408(11)	0.3534(8)	0.7401(9)	88(3)					
MO′	0.12952(9)	0.97526(6)	0.14008(8)	493(5)	458(5)	667(7)	−39(4)	−201(4)	51(4)
O2′	0.3521(9)	0.8627(7)	0.2502(8)	94(5)	126(7)	132(7)	6(5)	−63(5)	25(5)
O1′	−0.0536(10)	0.9835(8)	0.4193(8)	108(6)	126(7)	69(6)	10(5)	−11(5)	−3(5)
N1′	0.1872(7)	0.8148(5)	0.0412(7)	45(4)	48(3)	75(5)	1(3)	−13(3)	−7(3)
N2′	−0.0427(6)	0.8817(5)	0.1236(6)	43(3)	50(4)	76(5)	−1(3)	−20(3)	3(3)
C1′	0.0826(12)	1.1720(9)	0.1326(11)	87(3)					
C2′	0.0653(11)	1.1337(8)	0.0326(9)	77(3)					
C3′	0.2006(10)	1.0777(8)	−0.0458(9)	75(2)					
C4′	0.3030(11)	1.0836(9)	0.0069(10)	81(3)					
C5′	0.2337(15)	1.1441(12)	0.1204(13)	91(4)					
C6′	0.0133(13)	0.9783(10)	0.3158(13)	83(8)	71(7)	77(9)	3(5)	−25(7)	9(6)
C7′	0.2675(11)	0.9054(8)	0.2090(9)	71(6)	76(6)	78(7)	−8(5)	−20(5)	8(5)
C8′	0.0496(9)	0.7970(6)	0.0623(8)	50(4)	44(4)	61(6)	−2(3)	−23(4)	13(4)
C9′	0.0086(8)	0.6903(6)	0.0241(7)	53(2)					
C10′	−0.0051(10)	0.6826(8)	−0.0861(9)	74(2)					
C11′	−0.0496(14)	0.5839(11)	−0.1217(12)	92(4)					
C12′	−0.0630(11)	0.4924(9)	−0.0476(10)	84(3)					
C13′	−0.0508(12)	0.4967(9)	0.0604(10)	91(3)					
C14′	−0.0164(11)	0.5972(8)	0.0987(9)	79(3)					
C15′	0.3185(9)	0.7336(6)	−0.0114(8)	52(4)	44(4)	86(6)	−2(3)	−17(4)	3(4)
C16′	0.4402(9)	0.7872(6)	−0.1131(8)	56(2)					
C17′	0.5806(10)	0.7831(8)	−0.1093(9)	73(2)					
C18′	0.6930(12)	0.8311(9)	−0.2045(11)	90(3)					
C19′	0.6614(13)	0.8848(10)	−0.2946(12)	87(4)					
C20′	0.5266(13)	0.8874(9)	−0.3015(11)	95(3)					

(continued overleaf)

TABLE VIII *(continued)*

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
C21′	0.4140(11)	0.8373(8)	−0.2090(9)	75(2)					
C22′	−0.2051(8)	0.8863(7)	0.1593(9)	45(4)	58(5)	89(7)	−3(3)	−21(4)	12(4)
C23′	−0.2768(10)	0.8395(10)	0.2859(11)	59(6)	108(8)	120(9)	−10(5)	−14(6)	58(7)
C24′	−0.2682(8)	1.0050(6)	0.1448(7)	50(2)					
C25′	−0.2897(10)	1.0348(8)	0.0394(9)	73(2)					
C26′	−0.3430(11)	1.1472(9)	0.0228(10)	82(3)					
C27′	−0.3754(11)	1.2238(8)	0.1134(9)	89(3)					
C28′	−0.3555(12)	1.1960(10)	0.2183(11)	95(3)					
C29′	−0.3021(11)	1.0863(8)	0.2331(9)	76(2)					
H1	0.5628(11)	0.5666(8)	0.6660(9)	13(1)					
H2	0.2859(11)	0.5317(8)	0.7456(9)	13(1)					
H3	0.1763(11)	0.6214(8)	0.5922(9)	13(1)					
H4	0.3839(11)	0.7100(8)	0.4213(9)	13(1)					
H5	0.6185(11)	0.6861(8)	0.4698(9)	13(1)					
H10	0.0850(11)	0.2715(8)	0.7217(9)	16(1)					
H11	−0.0652(11)	0.1126(8)	0.7731(9)	16(1)					
H12	0.0595(11)	−0.0663(8)	0.6751(9)	16(1)					
H13	0.2497(11)	−0.0754(8)	0.4953(9)	16(1)					
H14	0.3951(11)	0.0876(8)	0.4287(9)	16(1)					
H15A	0.2902(11)	0.3652(8)	0.2978(9)	9(1)					
H15B	0.1587(11)	0.3007(8)	0.4219(9)	9(1)					
H17	0.2409(11)	0.5597(8)	0.2619(9)	16(1)					
H18	0.0863(11)	0.7355(8)	0.3091(9)	16(1)					
H19	−0.1286(11)	0.7578(8)	0.4967(9)	16(1)					
H20	−0.1816(11)	0.6062(8)	0.6356(9)	16(1)					
H21	−0.0321(11)	0.4293(8)	0.5853(9)	16(1)					
H22	0.4175(11)	0.1844(8)	0.6965(9)	9(2)					
H23A	0.6840(11)	0.1218(8)	0.6318(9)	13(2)					
H23B	0.7265(11)	0.2321(8)	0.5251(9)	13(2)					
H23C	0.6269(11)	0.1232(8)	0.5078(9)	13(2)					
H25	0.2846(11)	0.3122(8)	0.8644(9)	16(1)					
H26	0.3068(11)	0.4350(8)	1.0223(9)	16(1)					
H27	0.5442(11)	0.4892(8)	0.9880(9)	16(1)					
H28	0.7357(11)	0.4540(8)	0.8209(9)	16(1)					
H29	0.7339(11)	0.3326(8)	0.6672(9)	16(1)					
H1′	0.0020(11)	1.2125(8)	0.2033(9)	13(1)					
H2′	−0.0293(11)	1.1437(8)	0.0169(9)	13(1)					
H3′	0.2189(11)	1.0408(8)	−0.1256(9)	13(1)					
H4′	0.4095(11)	1.0495(8)	−0.0288(9)	13(1)					
H5′	0.2784(11)	1.1630(8)	0.1783(9)	13(1)					
H10′	0.0165(11)	0.7476(8)	−0.1426(9)	16(1)					
H11′	−0.0689(11)	0.5805(8)	−0.1982(9)	16(1)					
H12′	−0.0839(11)	0.4193(8)	−0.0740(9)	16(1)					
H13′	−0.0661(11)	0.4287(8)	0.1144(9)	16(1)					
H14′	−0.0104(11)	0.6005(8)	0.1808(9)	16(1)					
H15A	0.3579(11)	0.7059(8)	0.0590(9)	9(1)					
H15B	0.2885(11)	0.6616(8)	−0.0473(9)	9(1)					
H17′	0.6003(11)	0.7465(8)	−0.0394(9)	16(1)					
H18′	0.7965(11)	0.8246(8)	−0.2052(9)	16(1)					
H19′	0.7405(11)	0.9238(8)	−0.3580(9)	16(1)					
H20′	0.5068(11)	0.9248(8)	−0.3714(9)	16(1)					
H21′	0.3134(11)	0.8377(8)	−0.2128(9)	16(1)					
H22′	−0.2312(11)	0.8329(8)	0.1001(9)	9(2)					
H23A	−0.3951(11)	0.8439(8)	0.3120(9)	13(2)					
H23B	−0.2534(11)	0.8898(8)	0.3509(9)	13(2)					
H23C	−0.2312(11)	0.7531(8)	0.2881(9)	13(2)					
H25′	−0.2679(11)	0.9756(8)	−0.0254(9)	16(1)					
H26′	−0.3562(11)	1.1684(8)	−0.0548(9)	16(1)					
H27′	−0.4142(11)	1.3032(8)	0.1028(9)	16(1)					
H28′	−0.3822(11)	1.2537(8)	0.2850(9)	16(1)					
H29′	−0.2838(11)	1.0656(8)	0.3102(9)	16(1)					

TABLE IX. Coordinates and Thermal Parameters ($\times 10^3$, Mo $\times 10^4$, H $\times 10^2$).

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MO	0.27852(6)	0.49837(8)	0.18870(3)	564(3)	557(3)	515(3)	−42(6)	−8(4)	134(5)
O1	0.5702(7)	0.5896(6)	0.2087(4)	63(4)	94(5)	158(8)	−16(4)	−30(5)	25(5)
O2	0.4625(9)	0.3623(7)	0.1022(4)	106(6)	89(5)	138(7)	17(5)	47(6)	2(5)
N1	0.1747(7)	0.5468(5)	0.1090(3)	74(5)	53(4)	52(4)	−5(3)	−10(4)	5(3)
N2	0.2226(7)	0.6776(5)	0.1715(3)	60(4)	47(3)	53(4)	−4(4)	−13(4)	0(3)
C1	0.1044(9)	0.4955(8)	0.2622(5)	67(1)					
C2	0.0778(9)	0.4057(8)	0.2223(5)	67(1)					
C3	0.1866(9)	0.3281(8)	0.2243(5)	67(1)					
C4	0.2804(9)	0.3701(8)	0.2654(5)	67(1)					
C5	0.2296(9)	0.4735(8)	0.2888(5)	67(1)					
C1'	0.0629(19)	0.4405(22)	0.2319(11)	67(1)					
C2'	0.1359(19)	0.3414(22)	0.2162(11)	67(1)					
C3'	0.2560(19)	0.3405(22)	0.2490(11)	67(1)					
C4'	0.2571(19)	0.4391(22)	0.2850(11)	67(1)					
C5'	0.1377(19)	0.5010(22)	0.2744(11)	67(1)					
C6	0.4606(11)	0.5603(8)	0.2017(5)	85(7)	51(5)	92(8)	3(5)	2(6)	14(5)
C7	0.3936(11)	0.4110(8)	0.1343(5)	71(7)	49(5)	120(9)	4(5)	19(7)	17(6)
C8	0.1654(8)	0.6564(7)	0.1214(3)	62(5)	47(4)	50(5)	−4(4)	1(4)	−2(4)
C9	0.0995(9)	0.7435(7)	0.0830(3)	49(2)					
C10	−0.0300(10)	0.7873(8)	0.0988(4)	71(3)					
C11	−0.0912(12)	0.8686(9)	0.0617(5)	88(3)					
C12	−0.0272(11)	0.9063(9)	0.0118(5)	88(3)					
C13	0.0979(11)	0.8650(9)	−0.0045(5)	84(3)					
C14	0.1609(9)	0.7838(7)	0.0322(4)	64(2)					
C15	0.1291(9)	0.4902(9)	0.0548(3)	91(6)	65(5)	48(4)	−20(8)	0(4)	−14(6)
C16	0.0340(9)	0.3930(7)	0.0640(4)	59(2)					
C17	−0.1020(13)	0.4093(11)	0.0738(5)	99(4)					
C18	−0.1901(13)	0.3072(11)	0.0823(5)	104(4)					
C19	−0.1293(14)	0.2075(12)	0.0821(6)	113(4)					
C20	−0.0013(15)	0.1901(14)	0.0750(6)	125(5)					
C21	0.0846(13)	0.2822(10)	0.0635(5)	93(4)					
C22	0.2339(9)	0.7930(6)	0.1974(3)	54(5)	60(4)	57(5)	2(4)	9(4)	−11(4)
C23	0.2874(11)	0.7871(8)	0.2605(3)	99(7)	95(7)	48(5)	−16(7)	9(6)	−8(5)
C24	0.3209(8)	0.8737(7)	0.1607(3)	52(2)					
C25	0.4274(9)	0.8353(8)	0.1268(4)	64(2)					
C26	0.5051(12)	0.9119(9)	0.0940(5)	89(3)					
C27	0.4801(10)	1.0289(9)	0.0953(4)	80(3)					
C28	0.3732(13)	1.0677(11)	0.1271(5)	109(4)					
C29	0.2943(10)	0.9905(10)	0.1602(4)	87(3)					
H1	0.0448(9)	0.5636(8)	0.2703(5)	4(1)					
H2	−0.0051(9)	0.3987(8)	0.1969(5)	4(1)					
H3	0.1945(9)	0.2555(8)	0.2003(5)	4(1)					
H4	0.3678(9)	0.3320(8)	0.2758(5)	4(1)					
H5	0.2753(9)	0.5224(8)	0.3191(5)	4(1)					
H1'	−0.0272(19)	0.4647(22)	0.2159(11)	4(1)					
H2'	0.1047(19)	0.2812(22)	0.1866(11)	4(1)					
H3'	0.3270(19)	0.2780(22)	0.2460(11)	4(1)					
H4'	0.3324(19)	0.4596(22)	0.3120(11)	4(1)					
H5'	0.1136(19)	0.5750(22)	0.2935(11)	4(1)					
H10	−0.0762(10)	0.7603(8)	0.1357(4)	16(1)					
H11	−0.1827(12)	0.8996(9)	0.0719(5)	16(1)					
H12	−0.0724(11)	0.9655(9)	−0.0137(5)	16(1)					
H13	0.1427(11)	0.8923(9)	−0.0417(5)	16(1)					
H14	0.2526(9)	0.7543(7)	0.0213(4)	16(1)					
H15A	0.0833(9)	0.5494(9)	0.0295(3)	7(2)					
H15B	0.2105(9)	0.4596(9)	0.0337(3)	7(2)					
H17	−0.1407(13)	0.4892(11)	0.0752(5)	16(1)					
H18	−0.2902(13)	0.3142(11)	0.0876(5)	16(1)					

(continued overleaf)

TABLE IX *(continued)*

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
H19	−0.1871(14)	0.1375(12)	0.0883(6)	16(1)					
H20	0.0359(15)	0.1098(14)	0.0777(6)	16(1)					
H21	0.1823(13)	0.2679(10)	0.0547(5)	16(1)					
H22	0.1397(9)	0.8245(6)	0.1979(3)	5(2)					
H23A	0.2936(11)	0.8675(8)	0.2766(3)	7(1)					
H23B	0.3792(11)	0.7507(8)	0.2607(3)	7(1)					
H23C	0.2245(11)	0.7403(8)	0.2855(3)	7(1)					
H25	0.4491(9)	0.7508(8)	0.1258(4)	16(1)					
H26	0.5805(12)	0.8814(9)	0.0690(5)	16(1)					
H27	0.5396(10)	1.0841(9)	0.0733(4)	16(1)					
H28	0.3501(13)	1.1520(11)	0.1269(5)	16(1)					
H29	0.2170(10)	1.0210(10)	0.1841(4)	16(1)					

TABLE X. Coordinates and Thermal Parameters ($\times 10^3$, Mo $\times 10^4$, H $\times 10^2$).

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MO	0.71230(8)	0.20682(6)	0.31667(3)	522(3)	500(3)	515(3)	−39(5)	6(4)	−57(4)
O1	0.4208(7)	0.3168(7)	0.3023(3)	62(4)	111(7)	120(7)	9(5)	−12(4)	2(5)
O2	0.5105(9)	0.0850(9)	0.4000(4)	87(6)	146(9)	129(8)	−40(6)	17(6)	47(7)
N1	0.8479(8)	0.2454(6)	0.3884(3)	59(4)	43(4)	53(4)	1(3)	2(4)	−1(3)
N2	0.7896(9)	0.3765(6)	0.3270(3)	81(4)	49(3)	46(4)	−5(5)	−4(5)	2(3)
C1	0.8668(16)	0.1946(13)	0.2368(8)	65(2)					
C2	0.9095(16)	0.1097(13)	0.2749(8)	65(2)					
C3	0.7999(16)	0.0325(13)	0.2818(8)	65(2)					
C4	0.6896(16)	0.0697(13)	0.2480(8)	65(2)					
C5	0.7309(16)	0.1698(13)	0.2202(8)	65(2)					
C1′	0.8806(16)	0.1816(16)	0.2442(10)	65(2)					
C2′	0.8822(16)	0.0844(16)	0.2789(10)	65(2)					
C3′	0.7520(16)	0.0322(16)	0.2754(10)	65(2)					
C4′	0.6699(16)	0.0971(16)	0.2385(10)	65(2)					
C5′	0.7494(16)	0.1894(16)	0.2192(10)	65(2)					
C6	0.5322(10)	0.2782(9)	0.3078(4)	72(6)	70(6)	70(7)	−2(6)	−7(5)	−7(6)
C7	0.5904(12)	0.1313(10)	0.3709(5)	67(7)	75(7)	85(7)	−8(6)	0(6)	4(6)
C8	0.8699(9)	0.3528(7)	0.3732(3)	42(4)	50(5)	42(4)	−1(4)	9(4)	−6(4)
C9	0.9706(9)	0.4319(7)	0.4002(3)	52(2)					
C10	1.0994(11)	0.4453(9)	0.3756(5)	74(3)					
C11	1.1949(14)	0.5177(10)	0.4000(5)	89(3)					
C12	1.1619(12)	0.5738(10)	0.4473(5)	85(3)					
C13	1.0402(13)	0.5636(11)	0.4733(5)	97(4)					
C14	0.9367(12)	0.4890(9)	0.4502(5)	77(3)					
C15	0.9139(10)	0.1959(8)	0.4388(3)	84(6)	51(5)	43(4)	−2(5)	−8(4)	5(4)
C16	0.9710(9)	0.0781(7)	0.4265(4)	50(2)					
C17	1.1125(11)	0.0660(9)	0.4158(4)	67(3)					
C18	1.1706(12)	−0.0380(9)	0.4048(4)	82(3)					
C19	1.0924(12)	−0.1323(10)	0.4026(4)	80(3)					
C20	0.9495(11)	−0.1255(10)	0.4121(4)	74(3)					
C21	0.8900(11)	−0.0191(8)	0.4238(4)	65(3)					
C22	0.7774(10)	0.4938(7)	0.3054(3)	63(5)	53(4)	48(5)	−3(5)	1(5)	10(4)
C23	0.7306(12)	0.4886(8)	0.2425(3)	87(7)	79(6)	52(5)	6(6)	−5(6)	9(5)
C24	0.6858(9)	0.5671(7)	0.3418(3)	53(2)					
C25	0.6170(10)	0.5251(9)	0.3897(4)	67(3)					
C26	0.5390(12)	0.5965(10)	0.4231(5)	83(3)					
C27	0.5263(13)	0.7095(12)	0.4094(5)	93(3)					
C28	0.5843(13)	0.7514(11)	0.3638(5)	98(4)					
C29	0.6708(10)	0.6824(9)	0.3291(4)	79(3)					

(continued overleaf)

TABLE X *(continued)*

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
C30	0.8133(13)	0.1947(9)	0.4879(4)	171(12)	68(6)	57(5)	20(10)	17(7)	8(5)
H1	0.9235(16)	0.2611(13)	0.2238(8)	6(1)					
H2	1.0020(16)	0.1050(13)	0.2939(8)	6(1)					
H3	0.8004(16)	−0.0370(13)	0.3066(8)	6(1)					
H4	0.5974(16)	0.0314(13)	0.2444(8)	6(1)					
H5	0.6735(16)	0.2157(13)	0.1932(8)	6(1)					
H1′	0.9593(16)	0.2359(16)	0.2383(10)	6(1)					
H2′	0.9623(16)	0.0572(16)	0.3022(10)	6(1)					
H3′	0.7228(16)	−0.0390(16)	0.2957(10)	6(1)					
H4′	0.5718(16)	0.0804(16)	0.2278(10)	6(1)					
H5′	0.7179(16)	0.2502(16)	0.1923(10)	6(1)					
H10	1.1233(11)	0.4025(9)	0.3402(5)	10(1)					
H11	1.2882(14)	0.5281(10)	0.3823(5)	10(1)					
H12	1.2323(12)	0.6265(10)	0.4642(5)	10(1)					
H13	1.0210(13)	0.6077(11)	0.5088(5)	10(1)					
H14	0.8448(12)	0.4785(9)	0.4691(5)	10(1)					
H15	0.9944(10)	0.2450(8)	0.4497(3)	11(1)					
H17	1.1728(11)	0.1355(9)	0.4161(4)	10(1)					
H18	1.2728(12)	−0.0438(9)	0.3984(4)	10(1)					
H19	1.1362(12)	−0.2080(10)	0.3941(4)	10(1)					
H20	0.8907(11)	−0.1959(10)	0.4105(4)	10(1)					
H21	0.7880(11)	−0.0133(8)	0.4304(4)	10(1)					
H22	0.8698(10)	0.5321(7)	0.3072(3)	11(1)					
H23A	0.7218(12)	0.5680(8)	0.2272(3)	11(1)					
H23B	0.6391(12)	0.4490(8)	0.2399(3)	11(1)					
H23C	0.8008(12)	0.4455(8)	0.2198(3)	11(1)					
H25	0.6249(10)	0.4422(9)	0.3998(4)	10(1)					
H26	0.4913(12)	0.5657(10)	0.4576(5)	10(1)					
H27	0.4716(13)	0.7611(12)	0.4347(5)	10(1)					
H28	0.5674(13)	0.8331(11)	0.3532(5)	10(1)					
H29	0.7205(10)	0.7165(9)	0.2959(4)	10(1)					
H30A	0.8593(13)	0.1608(9)	0.5220(4)	11(1)					
H30B	0.7304(13)	0.1478(9)	0.4775(4)	11(1)					
H30C	0.7835(13)	0.2747(9)	0.4966(4)	11(1)					

TABLE XI. Atomic Coordinates and Thermal Parameters (×1000, Mo × 10 000).

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MO	0.20359(7)	0.29497(5)	0.18684(3)	406(3)	314(3)	402(4)	19(4)	7(4)	−23(4)
O1	−0.0837(5)	0.1911(6)	0.2080(3)	46(4)	92(5)	96(6)	−8(4)	10(4)	−7(4)
O2	−0.0100(7)	0.4215(6)	0.1111(3)	81(6)	138(7)	106(7)	45(5)	−11(5)	37(6)
N1	0.3229(6)	0.2533(4)	0.1113(3)	47(4)	27(3)	40(4)	4(3)	12(4)	5(3)
N2	0.2777(6)	0.1244(4)	0.1736(2)	49(4)	31(3)	30(4)	−11(3)	4(3)	1(3)
C6	0.0263(8)	0.2298(8)	0.2002(4)	39(5)	80(7)	58(7)	17(5)	1(5)	−26(5)
C7	0.0716(9)	0.3720(9)	0.1374(4)	50(6)	106(8)	56(7)	14(6)	3(5)	−25(6)
C8	0.3416(8)	0.1456(6)	0.1260(3)	41(5)	44(5)	27(5)	−4(4)	−4(4)	−7(4)
C15	0.3778(8)	0.3046(6)	0.0595(3)	75(6)	28(4)	48(5)	2(5)	11(5)	−2(4)
C22	0.2562(7)	0.0052(5)	0.1921(3)	48(5)	26(3)	61(6)	1(3)	3(5)	9(4)
C23	0.2091(9)	0.0043(6)	0.2553(3)	78(6)	53(5)	38(5)	−6(6)	7(6)	14(4)
C30	0.2631(9)	0.3107(7)	0.0138(3)	125(9)	53(6)	56(6)	−21(6)	−26(6)	5(5)
C31	0.5057(8)	0.2366(6)	0.2592(4)	64(6)	64(6)	88(7)	−8(5)	−21(6)	3(5)
C1	0.3895(5)	0.3170(4)	0.2526(2)	44(2)					
C2	0.2616(5)	0.3144(4)	0.2814(2)	50(2)					
C3	0.1847(5)	0.4114(4)	0.2643(2)	62(3)					
C4	0.2651(5)	0.4740(4)	0.2250(2)	51(2)					

(continued on facing page)

TABLE XI *(continued)*

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
C5	0.3917(5)	0.4157(4)	0.2178(2)	51(2)					
C9	0.4299(5)	0.0625(4)	0.0952(2)	40(2)					
C10	0.3890(5)	0.0181(4)	0.0431(2)	57(2)					
C11	0.4732(5)	−0.0592(4)	0.0147(2)	70(3)					
C12	0.5984(5)	−0.0922(4)	0.0383(2)	66(3)					
C13	0.6392(5)	−0.0478(4)	0.0904(2)	70(3)					
C14	0.5550(5)	0.0295(4)	0.1188(2)	59(3)					
C16	0.4440(5)	0.4171(3)	0.0725(2)	42(2)					
C17	0.3694(5)	0.5187(3)	0.0741(2)	50(2)					
C18	0.4361(5)	0.6216(3)	0.0855(2)	57(2)					
C19	0.5775(5)	0.6229(3)	0.0951(2)	65(3)					
C20	0.6521(5)	0.5213(3)	0.0935(2)	71(3)					
C21	0.5853(5)	0.4184(3)	0.0822(2)	58(3)					
C24	0.1597(4)	−0.0588(4)	0.1551(2)	36(2)					
C25	0.1486(4)	−0.1766(4)	0.1625(2)	52(2)					
C26	0.0636(4)	−0.2403(4)	0.1270(2)	72(3)					
C27	−0.0102(4)	−0.1863(4)	0.0842(2)	65(3)					
C28	0.0008(4)	−0.0685(4)	0.0768(2)	56(2)					
C29	0.0858(4)	−0.0048(4)	0.1123(2)	47(2)					
H2	0.2285(5)	0.2499(4)	0.3110(2)	98(25)					
H3	0.0828(5)	0.4337(4)	0.2787(2)	88(28)					
H4	0.2352(5)	0.5523(4)	0.2043(2)	81(27)					
H5	0.4751(5)	0.4418(4)	0.1906(2)	82(25)					
H10	0.2921(5)	0.0436(4)	0.0248(2)	160(18)					
H11	0.4416(5)	−0.0936(4)	−0.0256(2)	160(18)					
H12	0.6636(5)	−0.1521(4)	0.0163(2)	160(18)					
H13	0.7361(5)	−0.0733(4)	0.1087(2)	160(18)					
H14	0.5866(5)	0.0639(4)	0.1591(2)	160(18)					
H15	0.4522(8)	0.2559(6)	0.0432(3)	36(23)					
H17	0.2617(5)	0.5101(3)	0.0677(2)	123(14)					
H18	0.3739(5)	0.6928(3)	0.0926(2)	123(14)					
H19	0.6249(5)	0.6994(3)	0.1089(2)	123(14)					
H20	0.7637(5)	0.5233(3)	0.1003(2)	123(14)					
H21	0.6515(5)	0.3406(3)	0.0753(2)	123(14)					
H22	0.3458(7)	−0.0360(5)	0.1888(3)	27(18)					
H23A	0.1947(9)	−0.0762(6)	0.2680(3)	130(13)					
H23B	0.1211(9)	0.0477(6)	0.2590(3)	130(13)					
H23C	0.2812(9)	0.0410(6)	0.2793(3)	130(13)					
H25	0.1917(4)	−0.2242(4)	0.2023(2)	115(14)					
H26	0.0612(4)	−0.3395(4)	0.1330(2)	115(14)					
H27	−0.0595(4)	−0.2448(4)	0.0538(2)	115(14)					
H28	−0.0498(4)	−0.0346(4)	0.0439(2)	115(14)					
H29	0.0807(4)	0.0807(4)	0.1132(2)	115(14)					
H30A	0.3009(9)	0.3455(7)	−0.0216(3)	130(13)					
H30B	0.1855(9)	0.3584(7)	0.0281(3)	130(13)					
H30C	0.2292(9)	0.2319(7)	0.0054(3)	130(13)					
H31A	0.4789(8)	0.1742(6)	0.2858(4)	130(13)					
H31B	0.5869(8)	0.2784(6)	0.2747(4)	130(13)					
H31C	0.5297(8)	0.2031(6)	0.2216(4)	130(13)					

pyramid. For the minor (30%) image, however, a Cp carbon, C(5′), is found to eclipse C(6) in one of the carbonyl groups.

Assuming that the refined populations of the two Cp images represent a Boltzmann distribution of Cp fragments between two conformational states, the energy difference between the two states may be estimated as:

$$\log_e \frac{\text{pop(1)}}{\text{pop(2)}} = -\frac{\Delta G}{RT}.$$

For the two images in Benz II, ΔG = 1.4 kcal/mol.

TABLE XII. Bond Distances, Angles and Torsion Angles for Benz-I and Benz-II.

a) Bond distances (Å)

	Ia	Ib	II
Mo–N(1)	2.175(7)	2.173(6)	2.149(6)
Mo–N(2)	2.199(6)	2.190(7)	2.177(6)
Mo–C(6)	1.949(9)	1.956(14)	1.959(11)
Mo–C(7)	1.956(14)	1.936(11)	1.957(11)
O(1)–C(6)	1.159(10)	1.151(14)	1.146(11)
O(2)–C(7)	1.145(14)	1.178(11)	1.142(11)
N(1)–C(8)	1.300(11)	1.310(10)	1.299(9)
N(1)–C(15)	1.440(4)	1.456(9)	1.461(9)
N(2)–C(8)	1.295(11)	1.303(9)	1.291(9)
N(2)–C(22)	1.453(10)	1.474(9)	1.460(8)
C(8)–C(9)	1.52(1)	1.50(1)	1.48(1)
C(15)–C(16)	1.52(1)	1.52(1)	1.48(1)
C(22)–C(23)	1.54(1)	1.51(1)	1.52(1)
C(22)–C(24)	1.51(1)	1.51(1)	1.52(1)
C(9)–C(10)	1.38(1)	1.37(1)	1.42(1)
C(10)–C(11)	1.42(2)	1.42(2)	1.40(1)
C(11)–C(12)	1.40(2)	1.36(2)	1.37(1)
C(12)–C(13)	1.25(2)	1.34(1)	1.38(1)
C(13)–C(14)	1.44(2)	1.41(1)	1.40(1)
C(14)–C(9)	1.39(1)	1.38(1)	1.38(1)
	1.38 av	1.38 av	1.39 av
C(16)–C(17)	1.37(1)	1.39(1)	1.38(1)
C(17)–C(18)	1.38(1)	1.40(1)	1.48(1)
C(18)–C(19)	1.40(1)	1.35(2)	1.30(2)
C(19)–C(20)	1.36(1)	1.35(2)	1.30(2)
C(20)–C(21)	1.38(1)	1.40(1)	1.39(2)
C(21)–C(16)	1.39(1)	1.37(1)	1.37(1)
	1.38 av	1.38 av	1.36 av
C(24)–C(25)	1.37(2)	1.37(1)	1.38(1)
C(25)–C(26)	1.46(2)	1.38(1)	1.39(1)
C(26)–C(27)	1.37(2)	1.36(2)	1.37(1)
C(27)–C(28)	1.21(2)	1.35(1)	1.35(1)
C(28)–C(29)	1.38(2)	1.42(1)	1.40(1)
C(29)–C(24)	1.40(1)	1.38(1)	1.37(1)
	1.36 av	1.38 av	1.38 av
C(Cp)–H(Cp)	1.00	1.00	1.00
C(Ph)–H(Ph)	0.99	0.99	1.00
C(15)–H(15A,B)	1.08	1.08	1.00
C(22)–H(22)	1.08	1.08	1.00
C(23)–H(23A,B,C)	1.08	1.08	1.00

b) Additional bond distances for Ia and Ib (Å)

	Ia	Ib
Mo–C(1)	2.31(1)	2.34(1)
Mo–C(2)	2.39(1)	2.40(1)
Mo–C(3)	2.40(1)	2.38(1)
Mo–C(4)	2.33(1)	2.31(1)
Mo–C(5)	2.30(1)	2.31(1)
	2.35 av	2.35 av
C(1)–C(2)	1.40(1)	1.36(1)
C(2)–C(3)	1.42(1)	1.40(1)
C(3)–C(4)	1.39(1)	1.38(1)
C(4)–C(5)	1.39(2)	1.43(2)
C(5)–C(1)	1.42(1)	1.43(2)

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TABLE XII *(continued)*

c) Additional bond distances for II (Å)

Mo–C(1)	2.39(1)	Mo–C(1′)	2.39(3)
Mo–C(2)	2.38(1)	Mo–C(2′)	2.44(3)
Mo–C(3)	2.31(1)	Mo–C(3′)	2.38(3)
Mo–C(4)	2.28(1)	Mo–C(4′)	2.29(3)
Mo–C(5)	2.33(1)	Mo–C(5′)	2.29(3)
	2.34 av		2.36 av
C(Cp)–C(Cp)	1.40	C(Cp′)–C(Cp′)	1.40

d) Bond angles (°)

	Ia	Ib	II
N(1)–Mo–N(2)	59.2(2)	59.0(2)	58.8(2)
N(1)–Mo–C(6)	118.3(3)	119.3(4)	118.0(3)
N(1)–Mo–C(7)	83.7(4)	81.8(4)	83.3(4)
N(2)–Mo–C(6)	86.7(3)	86.4(4)	85.0(3)
N(2)–Mo–C(7)	124.2(4)	121.0(3)	121.7(3)
C(6)–Mo–C(7)	75.6(4)	75.9(4)	75.4(4)
Mo–C(6)–O(1)	178.1(9)	177.7(1.1)	175.6(9)
Mo–C(7)–O(2)	177.2(1.1)	179.6(7)	178.4(9)
MoN(1)–C(8)	94.4(5)	95.4(5)	96.1(5)
Mo–N(1)–C(15)	138.2(5)	137.3(5)	137.3(6)
Mo–N(2)–C(8)	93.4(5)	94.9(5)	95.0(5)
Mo–N(2)–C(22)	140.6(5)	142.2(5)	141.0(5)
C(8)–N(1)–C(15)	127.4(7)	126.2(6)	126.6(8)
C(8)–N(2)–C(22)	126.0(7)	122.9(7)	124.0(7)
N(1)–C(8)–N(2)	112.8(8)	110.5(7)	110.1(7)
N(1)–C(8)–C(9)	123.5(8)	123.2(7)	124.5(7)
N(2)–C(8)–C(9)	123.7(8)	126.2(7)	125.4(7)
N(1)–C(15)–C(16)	110.3(7)	110.6(6)	114.6(7)
N(2)–C(22)–C(24)	110.2(6)	110.0(6)	112.7(6)
C(23)–C(22)–C(24)	113.6(8)	113.9(7)	110.1(7)
C(23)–C(22)–H(22)	107.7(9)	105.5(9)	109.2(5)
C(9)–C(10)–C(11)	121.(1)	122.(1)	119.(1)
C(10)–C(11)–C(12)	115.(1)	117.(1)	121.(1)
C(11)–C(12)–C(13)	126.(1)	122.(1)	121.(1)
C(12)–C(13)–C(14)	119.(1)	120.(1)	118.(1)
C(13)–C(14)–C(9)	120.(1)	121.(1)	122.(1)
C(14)–C(9)–C(10)	119.(1)	118.(1)	119.(1)
C(16)–C(17)–C(18)	121.(1)	119.(1)	119.(1)
C(17)–C(18)–C(29)	120.(1)	120.(1)	117.(1)
C(18)–C(19)–C(20)	120.(1)	122.(1)	126.(2)
C(19)–C(20)–C(21)	120.(1)	119.(1)	120.(2)
C(20)–C(21)–C(16)	120.(1)	120.(1)	119.(1)
C(21)–C(16)–C(17)	119.(1)	120.(1)	119.(1)
C(24)–C(25)–C(26)	117.(1)	121.(1)	121.(1)
C(25)–C(26)–C(27)	117.(1)	119.(1)	121.(1)
C(26)–C(27)–C(28)	125.(1)	122.(1)	118.(1)
C(27)–C(28)–C(29)	122.(1)	119.(1)	121.(1)
C(28)–C(29)–C(24)	119.(1)	121.(1)	121.(1)
C(29)–C(24)–C(25)	120.(1)	118.(1)	118.(1)

e) Selected torsion angles (°)

A	B	C	D	Ia	Ib	II
Mo	N(1)	C(15)	H(15A)	–	–	179.69
Mo	N(1)	C(15)	H(15B)	−176.20	176.15	–

(continued overleaf)

TABLE XII *(continued)*

A	B	C	D	Ia	Ib	II
C(8)	N(1)	C(15)	H(15A)	–	–	–3.79
C(8)	N(1)	C(15)	H(15B)	5.69	11.13	–
Mo	N(1)	C(15)	C(16)	–55.86	–63.38	58.81
Mo	N(2)	C(22)	H(22)	162.08	159.15	–128.03
C(8)	N(2)	C(22)	H(22)	–17.90	–23.08	53.38
Mo	N(2)	C(22)	C(24)	45.91	42.13	114.26
N(1)	C(8)	C(9)	C(10)	–89.35	–92.32	105.01
N(2)	C(8)	C(9)	C(10)	91.20	90.53	–75.42
N(1)	C(15)	C(16)	C(17)	97.15	126.35	81.02
N(2)	C(22)	C(24)	C(25)	82.79	95.00	–30.63
N(1)	Mo	Cp	C(2)	–8.99	17.23	–
N(2)	Mo	Cp	C(3)	–13.11	14.10	–
N(1)	Mo	Cp	C(2)	–	–	6.45
N(2)	Mo	Cp	C(1)	–	–	1.98
N(1)	Mo	Cp′	C(2′)	–	–	–18.21
N(2)	Mo	Cp′	C(1′)	–	–	–23.85
C(6)	Mo	Cp′	C(5′)	–	–	7.79

TABLE XIII. Bond Distances, Angles and Torsion Angles for Benz-III.

a) Bond distances (Å)

Mo–N(1)	2.186(7)	Mo–N(2)	2.134(7)
Mo–C(6)	1.940(10)	Mo–C(7)	1.948(11)
O(1)–C(6)	1.174(11)	O(2)–C(7)	1.165(12)
N(1)–C(8)	1.323(9)	N(2)–C(8)	1.365(10)
N(1)–C(15)	1.466(10)	N(2)–C(22)	1.467(10)
C(8)–C(9)	1.48(1)	C(9)–C(10)	1.38(1)
		C(10)–C(11)	1.38(2)
C(15)–C(16)	1.51(1)	C(11)–C(12)	1.33(1)
C(15)–C(30)	1.51(1)	C(12)–C(13)	1.33(2)
C(22)–C(23)	1.55(1)	C(13)–C(14)	1.43(2)
C(22)–C(24)	1.50(1)	C(14)–C(9)	1.40(1)
			1.38 av
C(16)–C(17)	1.40(1)	C(24)–C(25)	1.40(1)
C(17)–C(18)	1.36(1)	C(25)–C(26)	1.37(1)
C(18)–C(19)	1.34(1)	C(26)–C(27)	1.37(2)
C(19)–C(20)	1.40(1)	C(27)–C(28)	1.31(1)
C(20)–C(21)	1.40(1)	C(28)–C(29)	1.42(1)
C(21)–C(16)	1.38(1)	C(29)–C(24)	1.39(1)
	1.38 av		1.38 av
Mo–C(1)	2.40(2)	Mo–C(1′)	2.38(2)
Mo–C(2)	2.42(2)	Mo–C(2′)	2.35(2)
Mo–C(3)	2.35(2)	Mo–C(3′)	2.29(2)
Mo–C(4)	2.29(2)	Mo–C(4′)	2.28(3)
Mo–C(5)	2.32(2)	Mo–C(5′)	2.33(3)
C–H	1.00	C(Cp)–C(Cp)	1.40

b) Bond angles (°)

N(1)–Mo–N(2)	60.7(2)	C(6)–Mo–C(7)	74.0(4)
N(1)–Mo–C(6)	122.1(3)	N(2)–Mo–C(7)	123.9(4)
N(1)–Mo–C(7)	87.0(4)	N(2)–Mo–C(6)	85.8(4)
Mo–C(6)–O(1)	177.2(1.0)	Mo–C(7)–O(2)	174.8(1.0)
Mo–N(1)–C(8)	94.7(6)	Mo–N(2)–C(8)	95.8(5)
Mo–N(1)–C(15)	143.6(6)	Mo–N(2)–C(22)	143.2(6)

TABLE XIII *(continued)*

N(1)–C(8)–N(2)	108.5(8)		
N(1)–C(8)–C(9)	125.4(8)	N(2)–C(8)–C(9)	126.0(7)
N(1)–C(15)–C(30)	110.1(8)	N(2)–C(22)–C(23)	108.6(7)
N(1)–C(15)–C(16)	111.3(7)	N(2)–C(22)–C(24)	112.5(7)
C(16)–C(15)–C(30)	110.9(8)	C(23)–C(22)–C(24)	113.4(8)
C(8)–C(9)–C(10)	118.7(8)	C(9)–C(10)–C(11)	120.(1)
C(8)–C(9)–C(14)	120.4(9)	C(10)–C(11)–C(12)	119.(1)
C(15)–C(16)–C(17)	119.0(9)	C(11)–C(12)–C(13)	123.(1)
C(15)–C(16)–C(21)	123.5(8)	C(12)–C(13)–C(14)	120.(1)
C(22)–C(24)–C(25)	122.7(8)	C(13)–C(14)–C(9)	117.(1)
C(22)–C(24)–C(29)	119.5(8)	C(14)–C(9)–C(10)	121.(1)
C(16)–C(17)–C(18)	122.(1)	C(24)–C(25)–C(26)	121.(1)
C(17)–C(18)–C(19)	120.(1)	C(25)–C(26)–C(27)	120.(1)
C(18)–C(19)–C(20)	120.(1)	C(26)–C(27)–C(28)	121.(1)
C(19)–C(20)–C(21)	119.(1)	C(27)–C(28)–C(29)	121.(1)
C(20)–C(21)–C(16)	121.(1)	C(28)–C(29)–C(24)	119.(1)
C(21)–C(16)–C(17)	118.(1)	C(29)–C(24)–C(25)	118.(1)

c) Selected torsion angles (°)

A	B	C	D	Angle
Mo	N(1)	C(15)	H(15)	159.36
Mo	N(1)	C(15)	C(30)	–82.58
Mo	N(1)	C(15)	C(16)	42.12
Mo	N(2)	C(22)	H(22)	–145.97
Mo	N(2)	C(22)	C(23)	–27.67
Mo	N(2)	C(22)	C(24)	98.64
N(1)	C(8)	C(9)	C(10)	97.02
N(2)	C(8)	C(9)	C(10)	–79.57
N(1)	C(15)	C(16)	C(17)	100.10
N(2)	C(22)	C(24)	C(25)	–3.19
N(1)	Mo	Cp	C(2)	–0.35
N(1)	Mo	Cp′	C(2′)	–0.65
N(2)	Mo	Cp	C(1)	–4.32
N(2)	Mo	Cp′	C(1′)	14.92

TABLE XIV. Bond Distances, Angles and Torsional Angles for Benz-IV.

a) Bond distances (Å)

Mo–N1 = 2.187(6)
Mo–N2 = 2.148(5)
Mo–C6 = 1.914(8)
Mo–C7 = 1.958(10)
01–C6 = 1.178(9)
02–C7 = 1.163(10)
N1–C8 = 1.322(8)
N2–C8 = 1.310(9)
N1–C15 = 1.466(9)
N2–C22 = 1.478(8)
C8–C9 = 1.491(8)

b) Bond angles (°)

N1–Mo–N2 = 59.7(2)
C6–Mo–C7 = 72.0(4)
N1–Mo–C6 = 121.7(3)
N2–Mo–C7 = 124.2(3)
N1–Mo–C7 = 87.5(3)
N2–Mo–C6 = 86.6(2)

Mo–C6–01 = 179.0(8)
Mo–C7–02 = 175.5(9)
Mo–N1–C8 = 94.0(5)
Mo–N2–C8 = 96.2(4)
Mo–N1–C15 = 141.7(5)
Mo–N2–C22 = 142.1(5)

N1–C8–N2 = 110.0(7)
N2–C8–C9 = 124.8(7)
N1–C8–C9 = 125.0(7)
N2–C22–C23 = 109.2(6)
N1–C15–C30 = 109.8(6)
N2–C22–C24 = 113.1(6)
N1–C15–C16 = 110.3(6)
C23–C22–C24 = 111.9(6)

c) Selected torsional angles (°)

A	B	C	D	Angle
Mo	N1	C15	H15	161.94
			C30	−81.34
			C16	45.39
	N2	C22	H22	−150.54
			C23	−32.05
			C24	93.33
N1	C8	C9	C10	107.12
N2	C8	C9	C10	−68.63
N1	C15	C16	C17	94.59
N2	C22	C24	C25	−7.58

N1–Mo–Cp–C1	−56.50
N1–Mo–Cp–C2	−128.47
N1–Mo–Cp–C3	159.41
N1–Mo–Cp–C4	87.45
N1–Mo–Cp–C5	15.41
N2–Mo–Cp–C1	11.19
N2–Mo–Cp–C2	−60.67
N2–Mo–Cp–C3	−132.80
N2–Mo–Cp–C4	155.24
N2–Mo–Cp–C5	83.30

Comparison of Benz I and Benz II

Figure 10 shows a Best Molecular Fit diagram comparing Benz IA with Benz II. By and large the conformations of the two molecules are remarkably similar, except at the optically active [H-C(CH_3)Ph] group which is oriented very differently. In Benz I (a preferred diastereoisomer) the Ph ring of [H-C-(CH_3)Ph] is very close to the Cp ring and the edge of the Cp ring faces the plane of the Ph ring. In Benz II, a non-preferred diastereoisomer, the Ph ring is as far away from the Cp ring as possible. In Fig. 10 the major (70%) Cp image was used to compare with Benz IA.

Crystal packing in Benz I

Benz I packs in space group P1, with two molecules in the asymmetric unit. The crystal packing is depicted in Fig. 11. From the figure, and from non-bonding contact distances listed in Table XIX, it appears that the major inter-molecular contacts involve Cp–Ph and Ph–Ph interactions similar to the intra-molecular interactions already discussed here and in refs. 3, 11, and 13.

Crystal packing in Benz II

As shown in Fig. 12, Benz II packs in space group $P2_12_12_1$ with four molecules in the unit cell. The non-bonding contacts (Table XX) also show some inter-molecular Cp–Ph interactions to be present in this compound.

Benz III and Benz IV

Molecular geometry

In most respects, Benz III and Benz IV (depicted in Figs. 13–16) resemble the other Mo–benzamidine complexes discussed above. Most bonding parameters (Table XIII and XIV) show only minor deviations from those listed for Benz I and Benz II (Table XII).

In Benz II, III and IV, the two N ligand sites are chemically identical though intramolecular changes in steric interactions cause the two Mo–N bond lengths to differ. Note that in Benz I, where the two side chains have approximately the same (preferred) conformation the two Mo–N distances are identical. Again, the two N–C(8) distances also differ significantly for II, III and IV but not in Benz I, which is symmetrical, as expected. The two N–Mo–C(O) *trans* angles (at the base of the square-pyramid) are almost equal, and the Mo–C(O) bond lengths are also equal.

For all Mo–benzamidine complexes, the phenyl rings are strictly planar. (See Tables XV–XVIII; for Benz I, II and III atoms were refined independently. In Benz IV, rigid body methods were used.) In Benz III, the Mo–N–C–N chelate ring is slightly bent (4.46°) about the N(1)–N(2) vector while in Benz IV, the relevant angle is 2.65°. The largest atomic deviations from the four-membered Mo–N–C–N ligand plane in Benz III and IV are, respectively, 0.036 Å and 0.016 Å. (In Benz IA, Benz IB and Benz II the largest deviations are 0.025, 0.015 and 0.009 Å). The angle between the aromatic N(1)–C(8)–N(2) fragment and the exocyclic [C(9)–C(14)] phenyl ring are 99.43° and 109.34° for III and IV, respectively.

The disordered Cp group The structure of Benz III was refined using two Cp images. As shown in Fig.

TABLE XV. Least-squares Plances, Lines and Deviations of Atoms from Those Planes for Benz-I.

Molecule A

a) Plane based on C(1) through C(5)
$(-0.0163)x + (-0.8496)y + (-0.5272)z = (-9.648)$

C(1)	0.0132	C(2)	−0.0046	C(3)	−0.0058
C(4)	0.0141	C(5)	−0.0169	Mo	2.018

b) Plane based on C(9) through C(14)
$(-0.7623)x + (0.2927)y + (-0.5772)z = (-7.039)$

C(9)	−0.0255	C(10)	−0.0115	C(11)	0.0544
C(12)	−0.0646	C(13)	0.0250	C(14)	0.0221

c) Plane based on C(16) through C(21)
$(-0.8352)x + (-0.3141)y + (-0.4514)z = (-6.938)$

C(16)	−0.0047	C(17)	0.0012	C(18)	−0.0008
C(19)	0.0041	C(20)	−0.0077	C(21)	0.0079

d) Plane based on C(24) through C(29)
$(-0.3503)x + (0.8239)y + (-0.4456)z = (-3.803)$

C(24)	−0.0002	C(25)	0.0008	C(26)	0.0066
C(27)	−0.0163	C(28)	0.0166	C(29)	−0.0074

e) Plane based on C(6), Mo and C(7)
$(-0.3829)x + (-0.9216)y + (-0.0640)z = (-8.347)$

f) Plane based on N(1), Mo and N(2)
$(-0.3829)x + (-0.9216)y + (-0.0640)z = (-8.347)$

g) Plane based on N(1), N(2) and C(8)
$(0.4080)x + (-0.4544)y + (-0.7919)z = (-3.637)$

h) Plane based on Mo, N(1), N(2) and C(8)
$(0.4008)x + (-0.4661)y + (-0.7888)z = (-3.730)$

Mo	−0.0095	N(1)	0.0173	N(2)	0.0172
C(8)	−0.0251				

i) Plane based on N(1), N(2), C(6) and C(7)
$(0.0449)x + (-0.8079)y + (-0.5876)z = (-6.264)$

N(1)	0.0530	N(2)	−0.0512	C(6)	0.0461
C(7)	−0.0479	Mo	−0.9928		

Equations of lines in orthogonal Å space

j) Line defined by Mo–Cp
$L(1) = I = (7.4625) + (-0.0288)T$
$L(2) = J = (6.4232) + (-0.8347)T$
$L(3) = K = (5.8162) + (0.5500)T$

k) Line defined by N(1)–N(2)
$L(1) = I = (6.5452) + (0.7589)T$
$L(2) = J = (3.9873) + (-0.3133)T$
$L(3) = K = (5.6770) + (0.5708)T$

Molecule B

a′) Plane based on C(1′) through C(5′)
$(0.1715)x + (0.8677)y + -(0.4666)z = (11.821)$

C(1′)	−0.0089	C(2′)	0.0071	C(3′)	−0.0022
C(4′)	−0.0031	C(5′)	0.0071	Mo′	−2.022

b′) Plane based on C(9′) through C(14′)
$(0.8372)x + (-0.3209)y + (-0.4428)z = (-1.823)$

C(9′)	0.0059	C(10′)	0.0239	C(11′)	−0.0388
C(12′)	0.0246	C(13′)	0.0061	C(14′)	−0.0217

c′) Plane based on C(16′) through C(21′)
$(-0.0106)x + (-0.8595)y + (-0.5110)z = (-7.406)$

TABLE XV *(continued)*

C(16′)	−0.0122	C(17′)	−0.0051	C(18′)	0.0221
C(19′)	−0.0219	C(20′)	0.0039	C(21′)	0.0131

d′) Plane based on C(24′) through C(29′)
$(0.8776)x + (0.2514)y + (-0.4082)z = (1.748)$

C(24′)	0.0026	C(25′)	−0.0061	C(26′)	0.0065
C(27′)	−0.0033	C(28′)	−0.0004	C(29′)	0.0007

e′) Plane based on C(6′), Mo′ and C(7′)
$(-0.4403)x + (-0.8951)y + (-0.0710)z = (-11.793)$

f′) Plane based on N(1′), Mo′ and N(2′)
$(-0.2098)x + (0.4966)y + (-0.8423)z = (3.745)$

g′) Plane based on N(1′), N(2′) and C(8′)
$(-0.2322)x + (0.4615)y + (-0.8562)z = (3.333)$

h′) Plane based on Mo′, N(1′), N(2′) and C(8′)
$(-0.2144)x + (0.4896)y + (-0.8452)z = (3.652)$

Mo′	−0.0060	N(1′)	0.0107	N(2′)	0.0107
C(8′)	−0.0154				

i′) Plane based on N(1′), N(2′), C(6′) and C(7′)
$(0.0763)x + (0.8477)y + (-0.5249)z = (8.170)$

N(1′)	−0.0249	N(2′)	0.0237	C(6′)	−0.0212
C(7′)	0.0224	Mo′	1.0070		

Equations of lines in orthogonal Å space

j′) Line defined by Mo′–Cp′
$L(1) = I = (3.2976) + (0.1196)T$
$L(2) = J = (12.3654) + (0.8626)T$
$L(3) = K = (1.0392) + (-0.4915)T$

k′) Line defined by N(1′)–N(2′)
$L(1) = I = (2.1870) + (-0.8319)T$
$L(2) = J = (10.0000) + (0.3620)T$
$L(3) = K = (0.9044) + (0.4206)T$

Angles between lines and/or planes

Equation 1	Equation 2	Angle° Molecule A	Angle° Molecule B
a	c	58.77	59.39
a	d	62.65	56.01
a	e	145.38	144.99
a	f	142.84	141.99
a	i	5.48	6.50
a	j	2.98	3.32
b	g	89.18	87.90
b	h	89.23	87.84
e	f	71.75	73.00
f	g	4.19	2.52
f	h	0.81	0.51
g	h	3.38	2.01

20, the two images (populations of 55 and 45%) are almost coincident. The C(2)–Cp(centroid)–Mo–N(1) torsion angles for the two images are −0.35 and −0.65°. Using the method already described for Benz II, the energy difference between the two Cp

TABLE XVI. Least-squares Planes, Lines and Deviations of Atoms from Those Planes for Benz-II.

a) Plane based on C(1) through C(5)
$(0.4589)x + (0.5136)y + (-0.7250)z = (-0.885)$
Mo 2.01

a′) Plane based on C(1′) through C(5′)
$(0.4586)x + (0.5136)y + (-0.7252)z = (-0.905)$
Mo 2.03

b) Plane based on C(9) through C(14)
$(-0.4320)x + (-0.7370)y + (-0.5198)z = (-7.733)$
C(9) 0.0035 C(10) −0.0025 C(11) 0.0028
C(12) −0.0039 C(13) 0.0048 C(14) −0.0047

c) Plane based on C(16) through C(21)
$(-0.1594)x + (-0.0707)y + (-0.9847)z = (-1.800)$
C(16) −0.0013 C(17) −0.0172 C(18) 0.0162
C(19) 0.0045 C(20) −0.0244 C(21) 0.0223

d) Plane based on C(24) through C(29)
$(-0.6098)x + (-0.1167)y + (-0.7839)z = (-5.953)$
C(24) −0.0088 C(25) 0.0018 C(26) 0.0115
C(27) −0.0180 C(28) 0.0110 C(29) 0.0024

e) Plane based on C(6), Mo and C(7)
$(-0.1572)x + (0.6877)y + (-0.7088)z = (0.500)$

f) Plane based on N(1), Mo and N(2)
$(0.8785)x + (0.1493)y + (-0.4538)z = (1.341)$

g) Plane based on N(1), N(2) and C(8)
$(0.8677)x + (0.1664)y + (-0.4685)z = (1.394)$

h) Plane based on Mo, N(1), N(2) and C(8)
$(0.8763)x + (0.1528)y + (-0.4568)z = (1.346)$
Mo −0.0034 N(1) 0.0061 N(2) 0.0060
C(8) −0.0087

i) Plane based on N(1), N(2), C(6) and C(7)
$(0.5067)x + (0.4744)y + (-0.7198)z = (2.066)$
N(1) 0.0313 N(2) −0.0305 C(6) 0.0270
C(7) −0.0277 Mo

Equations of lines in orthogonal Å space

j) Line defined by Mo–Cp
$L(1) = I = (2.2454) + (-0.5042)T$
$L(2) = J = (5.2708) + (-0.4805)T$
$L(3) = K = (4.9901) + (0.7176)T$

j′) Line defined by Mo–Cp′
$L(1) = I = (2.2164) + (-0.5276)T$
$L(2) = J = (5.2602) + (-0.4875)T$
$L(3) = K = (4.9763) + (0.6957)T$

k) Line defined by N(1)–N(2)
$L(1) = I = (1.9636) + (0.2234)T$
$L(2) = J = (7.0710) + (0.7113)T$
$L(3) = K = (3.1726) + (0.6664)T$

Angles between lines and/or planes

Equation 1	Equation 2	Angle°
a	a′	0.02
a	c	52.82
a	d	76.79

TABLE XVI *(continued)*

Equation 1	Equation 2	Angle°
a′	c	52.80
a′	d	76.77
a	e	142.65
a	f	143.98
a	i	3.56
a	j	3.22
a′	i	3.57
a′	j′	4.54
b	g	75.30
b	h	75.28
e	f	73.36
f	g	1.43
f	h	0.29
g	h	1.14
g	l	90.62
g	m	40.02
j	j′	1.83
j	k	88.64
j′	k	89.95

orientations in Benz III may be estimated as: $\Delta G \cong$ 0.7 kcal/mol. For Benz IV, the Me-Cp ring is fully ordered.

Comparison of Benz II, Benz III and Benz IV

Chemically, the only difference between Benz II, Benz III and Benz IV results from the substitution of a methyl group for one of the hydrogens on the CH_2Ph side group and the addition of a -CH_3 group to Cp in Benz IV. All three, however, share the common feature of being the non-preferred diastereoisomer. As shown in Fig. 22, substitution of hydrogen by methyl on the side chain leads to slightly longer N(1)–C(15) and C(15)–C(16) bond distances and greater angular distortions at the tetrahedral C(15) atom in Benz III. The two structures adopt similar conformations, in which the CH_2Ph group in Benz II and one of the (*S*)-CHMePh groups in Benz III have their phenyl rings facing respective Cp rings. As shown at the top of Fig. 22, the two remaining (*S*)-CHMePh groups adopt conformations typical of NP diastereomers. On this non-preferred side, the two Ph rings [C(24)–C(29)] differ only slightly in their orientations about their respective C(22)–C(24) vectors. Finally, one may note that for Benz II and III the two Cp images (only the major Cp image is plotted for each compound) are almost coincident, both having Cp carbons eclipsing the same nitrogens at the base of the square-pyramid (see Fig. 17). In Benz IV the single MeCp image adopts a similar conformation.

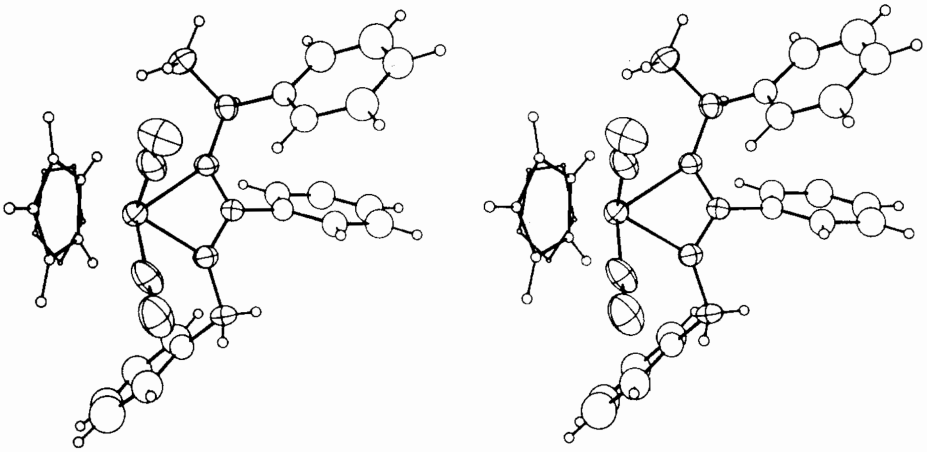


Fig. 8. Stereo view of Benz II.

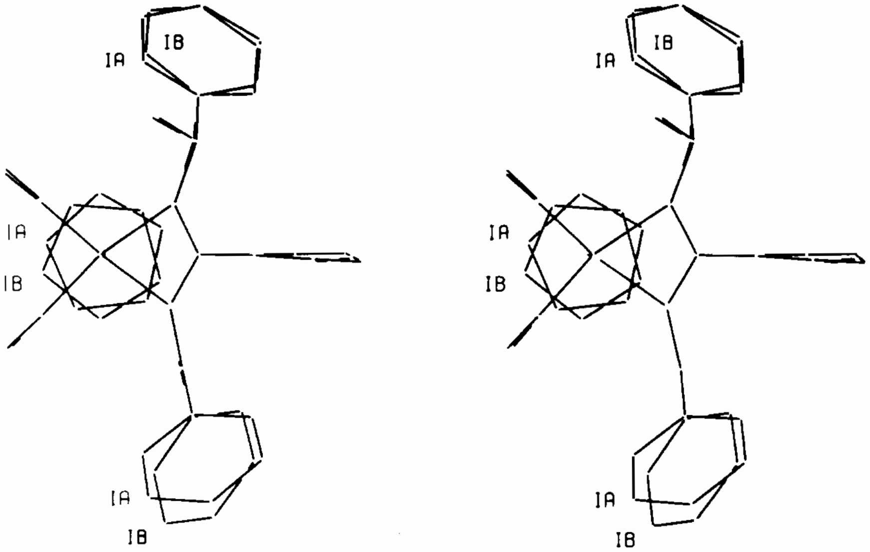


Fig. 9. BMFIT [35] diagram showing Benz Ia and Ib.

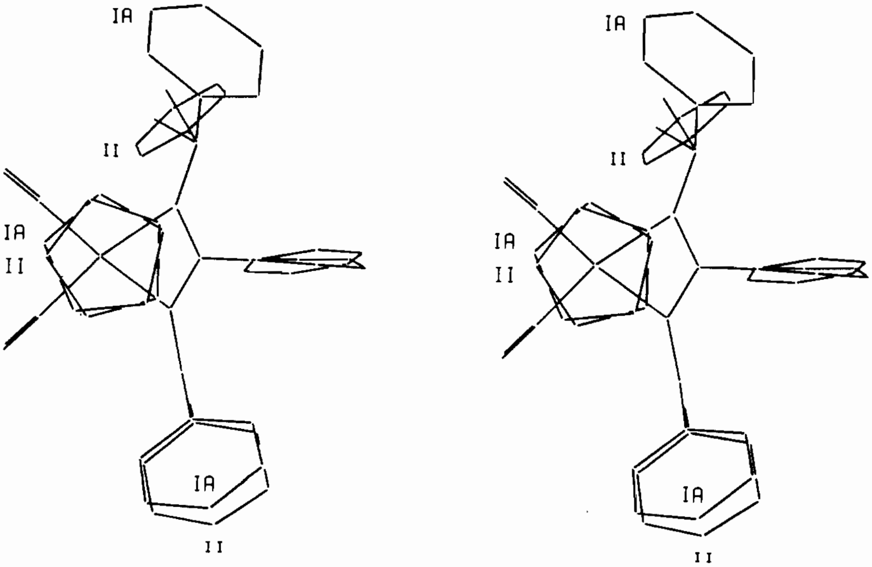


Fig. 10. BMFIT [35] diagram showing Benz Ia and Benz II. (Only the major, 70%, Cp image is shown for Benz II.)

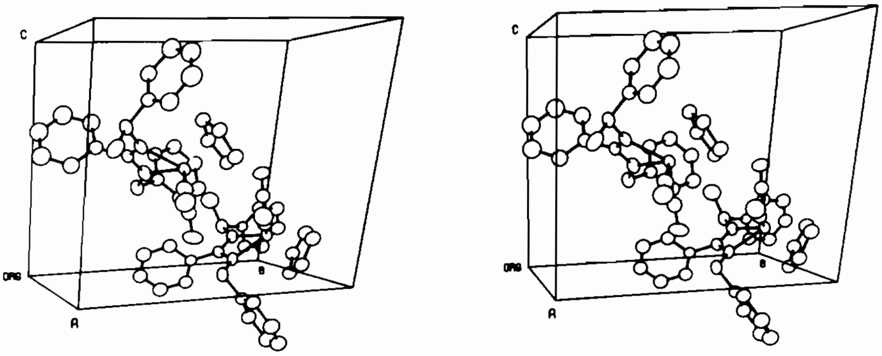


Fig. 11. Packing diagram for Benz I.

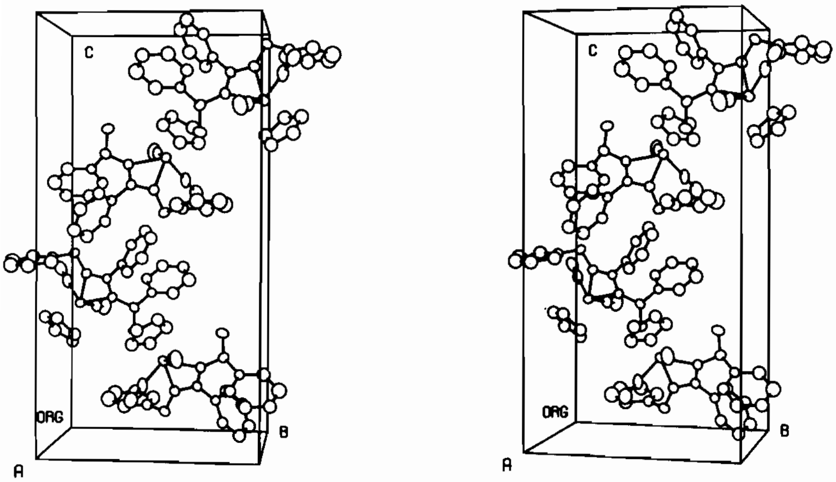


Fig. 12. Packing diagram for Benz II.

Crystal packing in Benz III and Benz IV

The similarities in molecular conformations adopted by Benz II, Benz III and Benz IV lead to similarities in crystal packing (see Figs. 12, 18 and 19). In Benz III the additional CH_3 at the optically active carbon group is directed along the c axis, and the entire molecule is shifted (with respect to Benz II, Fig. 18) along the a axis. Non-bonding contacts in Benz III (Table XXI) are similar to those listed for Benz II (Table XX) and differ from those of Benz IV (Table XXII) in those regions affected by the changes in torsional angles of the phenyl rings (see Fig. 20) and illustrated, for example, by the very short contact H25---O6 (2.57 Å) in Benz IV, which in Benz III is 3.36 Å. The fact that the methyl group in Benz IV occupies the very advantageous position it does (*i.e.*, minimum steric hindrance with the side chains) causes a torsional shift of the entire Cp ring (see BMFIT, Fig. 20) which, again causes shifts in the inter- and intramolecular contacts. However, the packing is, in general, remarkably similar as witnessed by the values of the Mo fractional coordinates (Tables X and XI).

Three rules, established on the basis of CpMo–thioamide stereochemistry [3, 11–13] may also be applied to these benzamidines. In all diastereoisomers, hydrogens on the optically active carbons are directed toward the exocyclic -Ph groups. As shown in Table XXIV, the intra-molecular Cp–Ph contacts displayed by Benz I through IV are similar to those listed for Mo–thioamides [13]: In Benz I, a P diastereoisomer; both independent molecules have their CH_2Ph and CHMePh side groups oriented with Ph rings facing the Cp groups; Benz II, however, has only one such interaction, that involving the -CH_2Ph side group. The NP diastereoisomer, Benz II, has its optically active -CHMePh side group oriented with its hydrogen (H) directed slightly out of the Mo–N–C–N (ligand) plane.

The significance of the additional N–CH_2Ph group in Benz I/Benz II as compared to the analogous Mo–thioamide compound (obtained by replacing N–CH_2Ph with (*S*)-CHMePh) may be examined on the basis of ^1H NMR data. For the pure diastereomers, Benz I and Benz II, Brunner, *et al.* [17] obtained H(Cp) peaks that differ by 0.66 ppm. The diastereomeric ratio (determined from another experiment) was 76:24. For P and NP diastereomers of the analogous Mo–thioamide compound, the H(Cp) peak deviation was 0.43 while the diastereomeric ratio was

TABLE XVII. Least-squares Planes, Lines and Deviations of Atoms from Those Planes for Benz-III.

a) Plane based on C(1) through C(5)
$(0.3479)x + (-0.5454)y + (-0.7626)z = (-2.583)$

Mo	−2.0319

a′) Plane based on C(1′) through C(5′)
$(0.3188)x + (-0.5511)y + (-0.7712)z = (-2.897)$

Mo	−1.9972

b) Plane based on C(9) through C(14)
$(-0.3584)x + (0.7593)y + (-0.5431)z = (-4.655)$

C(9)	0.0085	C(10)	−0.0035	C(11)	−0.0027
C(12)	0.0037	C(13)	0.0015	C(14)	−0.0074

c) Plane based on C(16) through C(21)
$(-0.1522)x + (0.1485)y + (-0.9771)z = (-11.102)$

C(16)	−0.0085	C(17)	0.0092	C(18)	−0.0041
C(19)	−0.0017	C(20)	0.0021	C(21)	0.0030

d) Plane based on C(24) through C(29)
$(-0.8024)x + (-0.2193)y + (-0.5551)z = (-11.236)$

C(24)	−0.0016	C(25)	0.0114	C(26)	−0.0035
C(27)	−0.0152	C(28)	0.0246	C(29)	−0.0156

e) Plane based on C(6), Mo and C(7)
$(-0.2427)x + (-0.6790)y + (-0.6929)z = (-8.481)$

f) Plane based on N(1), Mo and N(2)
$(0.7981)x + (-0.2321)y + (-0.5561)z = (0.779)$

g) Plane based on N(1), N(2) and C(8)
$(0.7401)x + (-0.2977)y + (-0.6030)z = (-0.314)$

h) Plane based on Mo, N(1), N(2) and C(8)
$(0.7861)x + (-0.2465)y + (-0.5668)z = (0.567)$

Mo	0.0150	N(1)	−0.0254	N(2)	−0.0252
C(8)	0.0356				

i) Plane based on N(1), N(2), C(6) and C(7)
$(0.3972)x + (-0.5348)y + (-0.7458)z = (-5.090)$

N(1)	−0.0179	N(2)	0.0184	C(6)	−0.0172
C(7)	0.0167	Mo	0.9645		

Equations of lines in orthogonal Å space

j) Line defined by Mo–Cp
$L(1) = I = (7.2984) + (0.4126)T$
$L(2) = J = (1.8826) + (-0.5257)T$
$L(3) = K = (6.7038) + (-0.7439)T$

j′) Line defined by Mo–Cp′
$L(1) = I = (7.2380) + (0.3598)T$
$L(2) = J = (1.8926) + (-0.5255)T$
$L(3) = K = (6.6907) + (-0.7709)T$

k) Line defined by N(1)–N(2)
$L(1) = I = (7.9063) + (-0.2581)T$
$L(2) = J = (3.6355) + (0.7023)T$
$L(3) = K = (8.4288) + (-0.6635)T$

Angles between lines and/or planes

TABLE XVII *(continued)*

Equation 1	Equation 2	Angle°
a	a′	1.77
a	c	52.32
a	d	74.71
a′	c	51.45
a′	d	72.95
a	e	144.51
a	f	145.92
a	i	3.04
a	j	4.00
a′	i	4.82
a′	j′	2.78
b	g	99.43
b	h	99.27
e	f	69.56
f	g	5.70
f	h	1.24
g	h	4.46
j	j′	3.46
j	k	88.98
j′	k	87.16

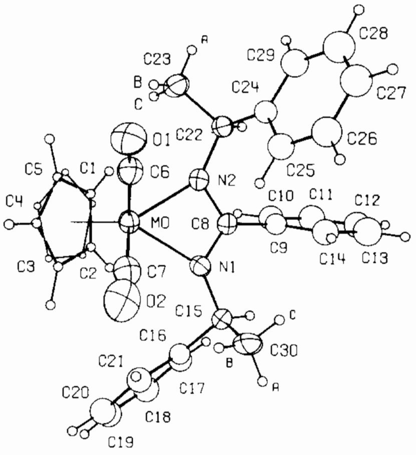


Fig. 13. Absolute configuration of Benz III.

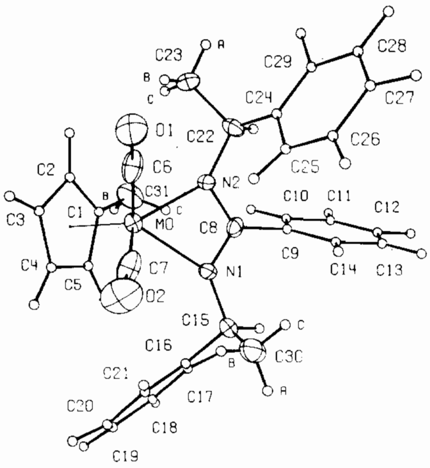


Fig. 14. Absolute configuration of Benz IV.

TABLE XVIII. Least-squares Planes, Lines and Deviations of Atoms from Those Planes for Benz-IV.

a) Plane based on C(1) through C(5)
(−0.3967)x + (−0.5280)y + (−0.7509)z = (−7.954)
Mo −2.0234

b) Plane based on C(9) through C(14)
(0.4547)x + (0.7584)y + (−0.4671)z = (1.407)

c) Plane based on C(16) through C(21)
(0.1609)x + (0.1300)y + (−0.9784)z = (−0.348)

d) Plane based on C(24) through C(29)
(0.7644)x + (−0.1394)y + (−0.6294)z = (−1.026)

e) Plane based on C(6), Mo and C(7)
(0.1704)x + (−0.6811)y + (−0.7121)z = (−5.164)

f) Plane based on N(1), Mo and N(2)
(−0.8437)x + (−0.2285)y + (−0.4857)z = (−4.610)

g) Plane based on N(1), N(2) and C(8)
(−0.8198)x + (−0.2596)y + (−0.5104)z = (−4.692)

h) Plane based on Mo, N(1), N(2) and C(8)
(−0.8390)x + (−0.2351)y + (−0.4908)z = (−4.639)
Mo −0.0065 N(1) 0.0112 N(2) 0.0116 C(8) −0.0163

Equations of lines in orthogonal Å space

i) Line defined by Mo–Cp
L(1) = I = (2.4444) + (0.4557)T
L(2) = J = (3.9920) + (0.5287)T
L(3) = K = (5.1470) + (0.7161)T

j) Line defined by N(1)–N(2)
L(1) = I = (2.9236) + (−0.2040)T
L(2) = J = (2.2122) + (−0.7004)T
L(3) = K = (3.3709) + (0.6839)T

Angles between lines and/or planes

Equation 1	Equation 2	Angle°
a	c	52.98
a	d	75.94
a	e	145.77
a	f	145.09
a	i	3.93
b	g	113.20
b	h	109.30
e	f	69.04
f	g	2.65
f	h	0.47
g	h	2.07
i	j	88.48

78:22 [39]. Thus, although the added CH_2Ph group may lead to greater perturbation of H(Cp) NMR signals, it *does not* contribute to an increased diastereomeric ratio.

TABLE XIX. Selected Non-bonding Contacts (Å) for Benz-I.

a) Intra-molecular

Atom 1	Atom 2	Dist.	Atom 1	Atom 2	Dist.
O(1)	H23B)	2.61	O(1′)	H(23B′)	2.74
O(2)	H(15A)	3.22	O(2′)	H(15A′)	2.97
C(6)	H(23B)	2.68	C(6′)	H(23B′)	2.80
C(7)	H(15A)	3.02	C(7′)	H(15A′)	2.86
C(9)	H(15B)	2.57	C(9′)	H(15B′)	2.52
C(9)	H(22)	2.55	C(9′)	H(22′)	2.60
Cp[a]	Ph(2)	4.60	Cp′	Ph(2′)	4.86
H(3)	Ph(2)	2.70	H(4′)	Ph(2)	3.18
H(3)	C(21)	2.78	H(4′)	C(16′)	3.25
Cp	Ph(3)	4.52	Cp′	Ph(3′)	4.62
H(1)	Ph(3)	2.94	H(2′)	Ph(3′)	2.71
H(1)	C(29)	2.78	H(2′)	C(25′)	2.91

b) Inter-molecular

		Symmetry Operation[b]			
Atom 1	Atom 2	x	y	z	Dist.
O(1)	H(13′)	1	1	0	2.81
O(2)	H(27)	0	0	−1	2.65
O(1′)	H(19′)	−1	0	1	2.77
O(2′)	H(13)	0	1	0	2.78
H(23A)	H(19′)	0	−1	1	2.37
H(23C)	H(29′)	1	−1	0	2.27
H(23C)	H(5)	−1	0	0	2.27
Cp	Ph(2′)	0	0	1	4.35
Cp	H(21′)	0	0	1	3.40
C(1)	C(21′)	0	0	1	3.39
Cp	Ph(1′)	0	0	1	5.13
H(2)	Ph(1′)	0	0	1	3.34
H(2)	C(11′)	0	0	1	3.05
H(3)	H(11′)	0	0	1	2.79
Ph(3)	Ph(3′)	1	−1	1	5.14
Ph(3)	H(26′)	1	−1	1	3.11
C(27)	H(27′)	1	−1	1	2.83
C(28)	H(26′)	1	−1	1	3.26
C(29)	H(26′)	1	−1	1	3.24
Cp′	Ph(3′)	1	0	0	5.32
H(4′)	C(26′)	1	0	0	3.07
Ph(2)	Ph(2′)	−1	0	1	5.53
H(19)	C(19′)	−1	0	1	2.88
H(20)	C(18′)	−1	0	1	3.17

[a] Cp and Cp′ denote the centroids of cyclopentadienyl rings in the two independent molecules. Ph(1), Ph(2), Ph(3) and Ph(1′), Ph(2′), Ph(3′) denote the centroids of phenyl groups. [b] The second atom has been moved through an (x, y, z) translation prior to the distance calculation.

Chirality Indicators, Configurations and CD Spectra

As a final point of discussion, one may examine the relationships between assigned (*R*,*S*) chirality indicators, actual configurations and circular dichroism (CD) spectra for Mo–thioamides and Mo–benzamidines.

For the original [3] preferred (P) Mo–thioamide structure, 7, the priority sequence [2, 3]:

TABLE XX. Selected Non-bonding Contacts (Å) for Benz-II.

a) Intra-molecular

Atom 1	Atom 2	Dist.	Atom 1	Atom 2	Dist.
C(1)	C(1′)	0.43	C(4)	C(4′)	0.56
C(2)	C(2′)	0.48	C(5)	C(5′)	0.49
C(3)	C(3′)	0.55	Cp[a]	Cp′	0.07
O(1)	H(23B)	2.90	O(2)	H(15B)	3.14
C(6)	H(23B)	2.69	C(7)	H(15B)	2.96
C(9)	H(22)	2.79	C(9)	H(15A)	2.55
C(9)	C(24)	3.18	C(14)	C(25)	3.45
Ph(1)	Ph(3)	4.29	C(14)	H(25)	3.57
Cp	Ph(2)	4.82	Cp′	Ph(2)	4.76
H(2)	Ph(2)	2.99	H(3′)	Ph(2)	2.99
H(2)	C(17)	2.95	H(3′)	C(21)	2.79
H(2)	C(16)	3.03	H(3′)	C(20)	2.93

b) Inter-molecular

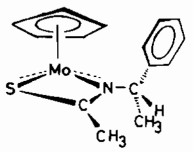
		Symmetry Operation[b]				
Atom 1	Atom 2	R	x	y	z	Dist.
O(1)	H(3′)	2	1	0	0	2.61
O(2)	H(18)	1	1	0	0	2.53
H(15A)	H(26)	4	−1	1	0	2.37
H(15B)	H(12)	4	0	1	0	2.36
Cp	Ph(3)	2	1	−1	0	5.01
H(4)	Ph(3)	2	1	−1	0	3.46
H(4)	C(25)	2	1	−1	0	2.99
Cp′	Ph(3)	2	1	−1	0	5.09
H(5′)	Ph(3)	2	1	−1	0	2.98
H(5′)	C(25)	2	1	−1	0	3.10
Cp	Ph(1)	2	0	−1	0	5.09
Cp′	Ph(1)	2	0	−1	0	5.09
Ph(1)	Ph(3)	4	−1	1	0	5.25
Ph(2)	Ph(3)	4	0	1	0	5.41
Ph(1)	Ph(2)	1	0	1	0	5.55

[a] Cp and Cp′ denote the ring centroids of the disordered cyclopentadienyl group. Ph(1), Ph(2) and Ph(3) denote the centroids of the three phenyl groups. [b] The second atom has been moved by rotation and/or inversion operator (R) and by (x, y, z) unit cell translations prior to distance calculation. The rotation operators are:

1) x, y, z
2) −x, 1/2 + y, 1/2 − z
3) 1/2 − x, −y, 1/2 + z
4) 1/2 + x, 1/2 − y, −z

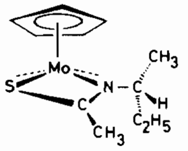
$$(\eta^5\text{-}C_5H_5) > S > N\text{-}CH(CH_3)C_6H_5 > C(O)$$

may be used to assign the chirality indicator (*S*) at the Mo site. By coincidence, this (*S*;C)(*S*;Mo) diastereomer was found to display a negative (−) rotational amplitude in its CD spectrum in the region of 578 nm [3]. The correlation between configuration at Mo and sign of rotation in this region was confirmed in two other diastereomers for which absolute configurations were determined. Elsewhere [13], this correlation was stated as a general rule for Mo–thioamides.



(7)

Among the Mo–thioamide complexes *examined thus far*, it was also observed that a chirality of (*S*) at carbon induces the same (*S*) chirality at the Mo site in preferred (P) diastereomers. This relationship appears to be completely general; however, it is possible it may not apply to all Mo–thioamides. The compound below (8) represents one Mo–thioamide compound which has been synthesized [39c]

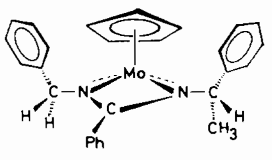


(8)

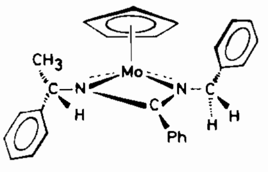
but which has not been structurally characterized as yet. Nonetheless, according to the rules established earlier [13], the preferred (P) diastereomer of this compound *should* have a structure similar to 8, where the minimization of intra-molecular repulsive forces requires the larger alkyl group (on the optically active carbon) to be directed away from the bulky Cp ring. Since structures 7 and 8 are identical at their Mo sites, the chirality at Mo in 8 may be designated (*S*). The C site in 8 is different, however, in that a direct application of the Cahn–Ingold–Prelog [40] system of nomenclature would use the priority sequence:

$$N > C_2H_5 > CH_3 > H$$

to assign the chirality indicator (*R*) to carbon. Thus, although both 7 and 8 represent preferred (P) diastereomers, the chirality of 7 is (*S*;C)(*S*;Mo), while that for 8 is (*R*;C)(*S*;Mo). Whereas individual molecular features may identify diastereomers as P or NP, chirality designators are *assigned* on the basis of systematic, but arbitrary rules.



(9)



(10)

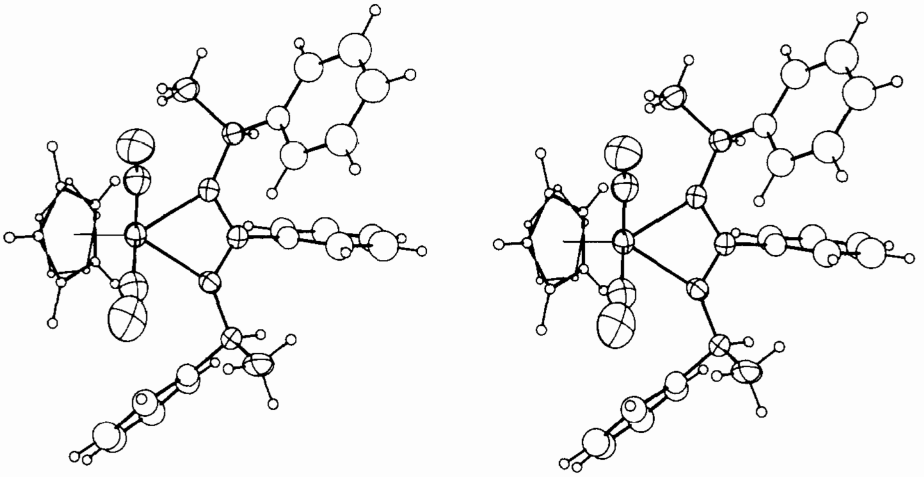


Fig. 15. Stereo view of Benz III.

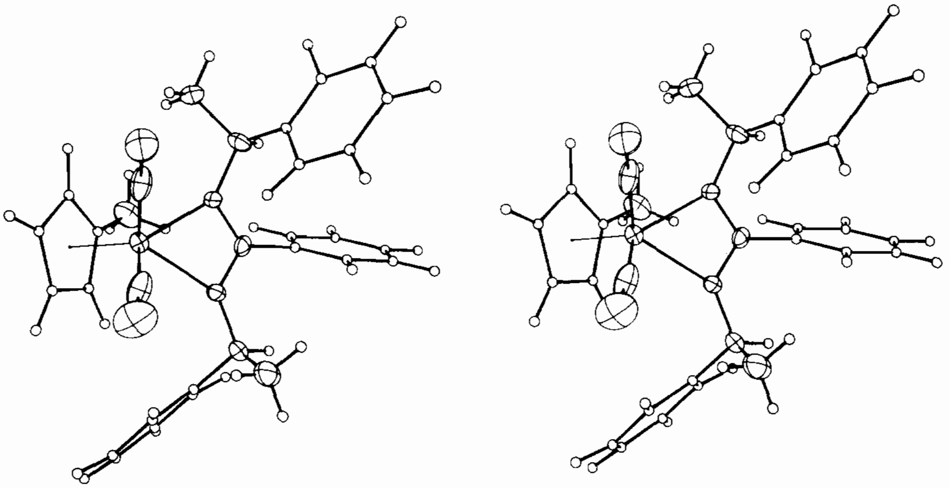


Fig. 16. Stereo view of Benz IV.

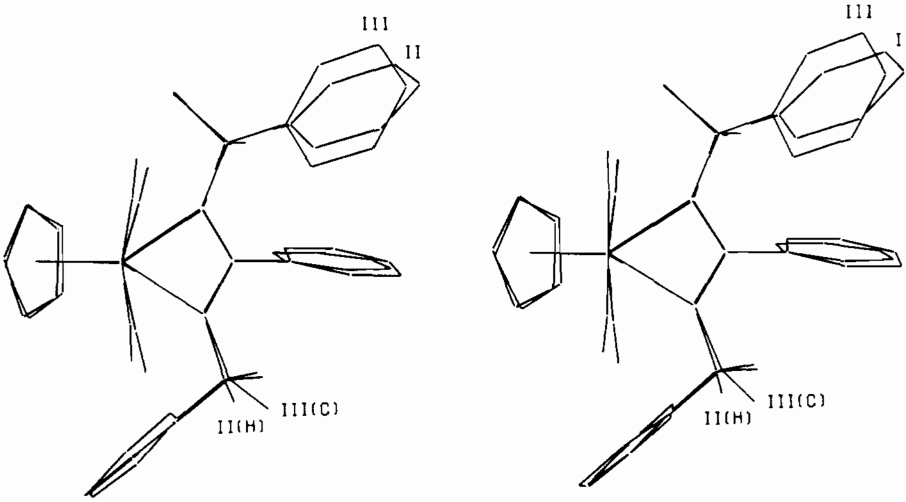


Fig. 17. BMFIT [35] diagram showing Benz II and Benz III. (For each compound only the major Cp image is depicted.)

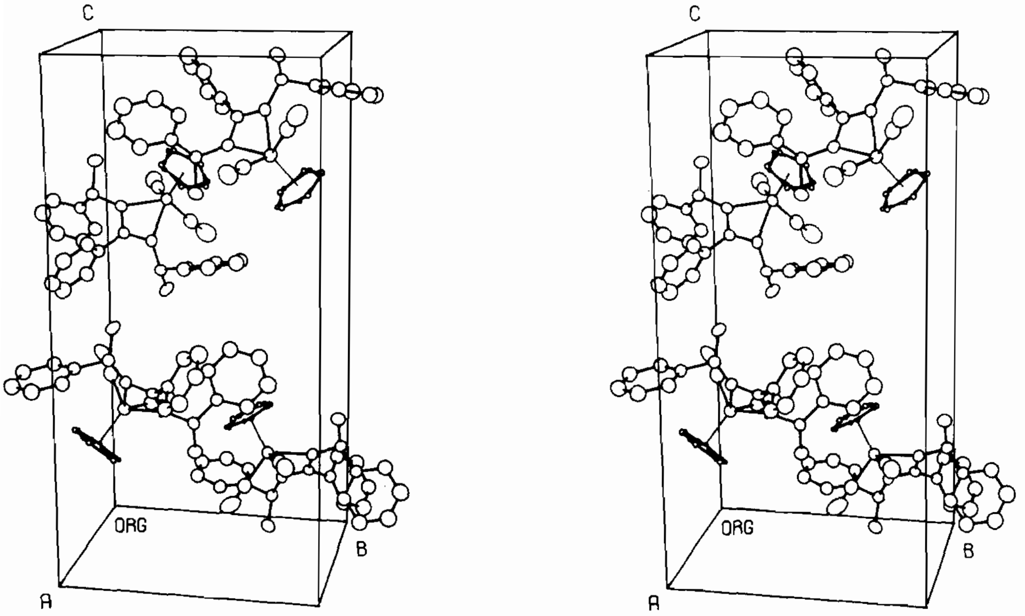


Fig. 18. Packing diagram for Benz III.

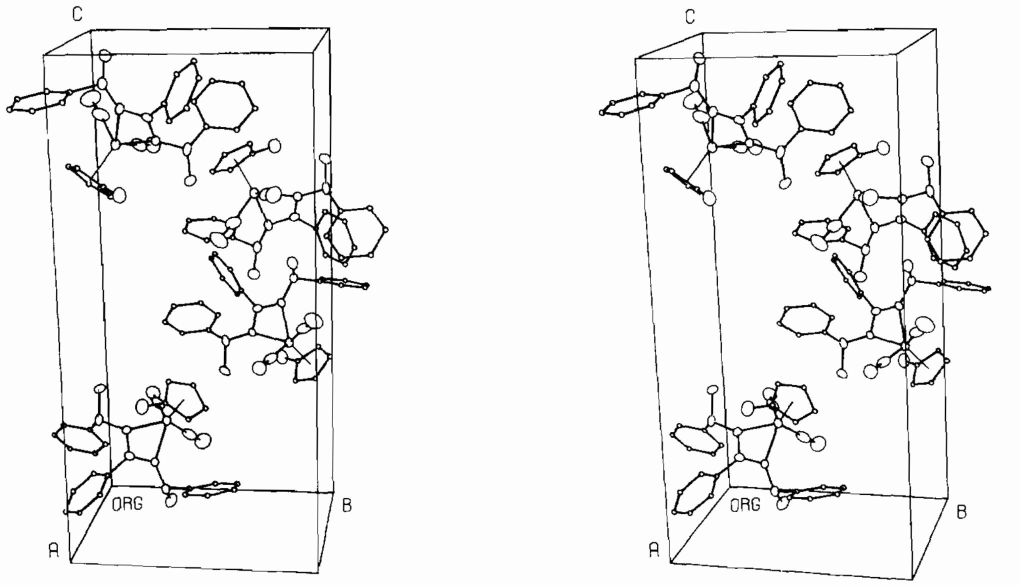
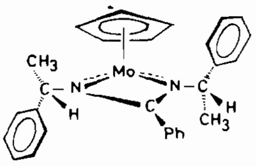


Fig. 19. Packing diagram for Benz IV.

Structures 9 and 10 represent the P and NP diastereomers Benz I and Benz II. These compounds differ from Mo–thioamides in that they have a second nitrogen site (rather than S) in the base of the square pyramid. In the P diastereomer, 9, the priority sequence:

$(\eta^5\text{-}C_5H_5) > \text{N-CH}(CH_3)C_6H_5 > \text{N-}CH_2C_6H_5 > \text{C(O)}$

may be used to assign the chirality indicator (*R*) at the Mo site; the C site, however, has a chirality of (*S*). In the NP diastereomer, 10, the chirality is (*S*;C)(*S*;Mo). The CD spectra for 9 and 10 have rotational amplitudes of (–) and (+), respectively, in the region of 578 nm. Thus, the correlation between chirality at Mo and sign of rotation in Mo–benzamidines is the reverse of that stated for Mo–thioamides.



(11)

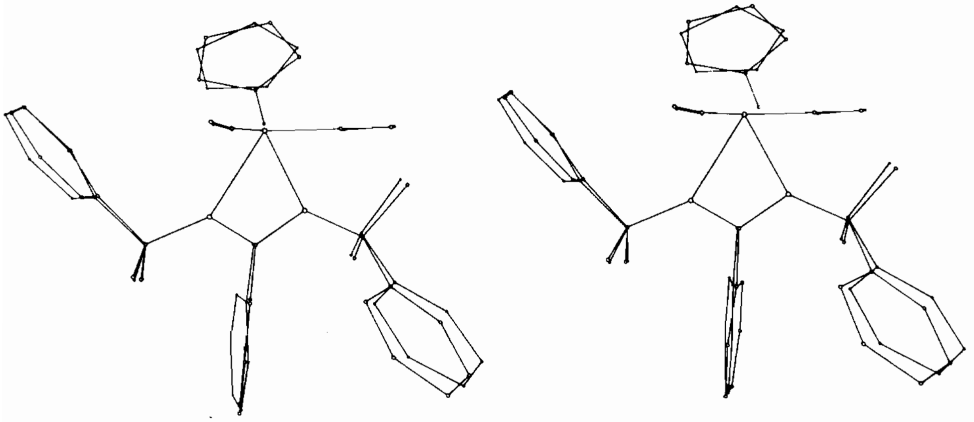


Fig. 20. BMFIT [35] diagram showing Benz II and Benz IV.

TABLE XXI. Selected Non-bonding Contacts (Å) for Benz III.

a) Intra-molecular

Atom 1	Atom 2	Dist.	Atom 1	Atom 2	Dist.
C(1)	C(1′)	0.26	C(4)	C(4′)	0.43
C(2)	C(2′)	0.41	C(5)	C(5′)	0.29
C(3)	C(3′)	0.49	Cp[a]	Cp′	0.12
O(1)	H(23B)	3.00	O(2)	H(30B)	2.90
C(6)	H(23B)	2.76	C(7)	H(30B)	2.86
C(9)	H(22)	2.67	C(9)	H(15)	2.49
Cp	Ph(2)	4.73	Cp′	Ph(2)	4.82
H(2)	Ph(2)	3.25	H(2′)	Ph(2)	2.90
H(2)	C(16)	3.15	H(2′)	C(16)	2.94
H(2)	C(17)	3.10	H(2′)	C(17)	3.04
H(3)	C(21)	2.90	H(3′)	C(21)	3.43
Ph(1)	Ph(3)	4.88	C(14)	H(25)	3.28
C(9)	C(24)	3.46	C(14)	C(25)	3.43

b) Inter-molecular

Symmetry Operation[b]

Atom 1	Atom 2	R	x	y	z	Dist.
O(1)	H(4)	2	1	0	0	2.74
O(2)	H(18)	1	−1	0	0	2.75
H(23B)	H(4)	2	1	0	0	2.50
H(30C)	H(17)	4	−1	0	1	2.54
Cp′	Ph(3)	2	1	−1	0	4.83
H(4′)	Ph(3)	2	1	−1	0	3.05
H(4′)	C(24)	2	1	−1	0	2.98
H(4′)	C(29)	2	1	−1	0	2.95
Cp	Ph(3)	2	1	−1	0	4.94
H(5)	Ph(3)	2	1	−1	0	3.26
H(5)	C(24)	2	1	−1	0	3.96
H(5)	C(29)	2	1	−1	0	2.39
Cp	Ph(1)	2	2	−1	0	4.55
Cp′	Ph(1)	2	2	−1	0	4.57
Ph(2)	Ph(3)	4	0	0	1	5.15
Ph(1)	Ph(2)	1	0	1	0	5.49
Ph(1)	Ph(3)	1	1	0	0	5.53

[a] Cp and Cp′ denote the ring centroids of the disordered cyclopentadienyl group. Ph(1), Ph(2) and Ph(3) denote the centroids of the three phenyl groups. [b] The second atom has been moved by rotation and/or inversion operator (R) and by (x, y, z) unit cell translations prior to distance calculation. The rotation operators are:
1) x, y, z
2) −x, 1/2 + y, 1/2 − z
3) 1/2 − x, −y, 1/2 + z
4) 1/2 + x, 1/2 − y, z

For the compounds examined thus far, strong CD rotational amplitudes in the region of 578 nm have been characteristic of chiral metal sites. The compound Benz III (structure 11) is interesting because formally it has only two chiral sites (both at carbon atoms). Nonetheless, it also displays a strong (−) rotational amplitude at 578 nm due to conformational effects which must persist in solution. Comparison of structures 10 and 11 (Benz II and Benz III) show them to differ in only one feature: H in 10 is replaced by CH_3 in 11. Both compounds adopt the same conformation, in which one phenyl group is directed up toward the Cp ligand while a second phenyl group is directed toward a carbonyl. Whereas the orientation of the optically active side group in Benz II, 10 identifies it as a nonpreferred (NP) diastereomer, Benz III, 11 must be labeled as a 'mixed' compound, since its two optically active side groups assume both P and NP orientations with respect to its $CpMo(CO)_2$ fragments.

Acknowledgements

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TABLE XXII. Selected Non-bonding Contacts (Å) for Benz-IV.

a) Intra-molecular

Atom 1	Atom 2	Dist.	Atom 1	Atom 2	Dist.
O(1)	H(23B)	2.99	O(2)	H(30B)	2.83
C(6)	H(23B)	2.71	C(7)	H(30B)	2.82
C(9)	H(22)	2.63	C(9)	H(15)	2.59
H(5)	Ph(2)	2.71	C(9)	C(24)	3.31
H(5)	C(16)	2.82	C(8)	H(31E)	2.99
H(5)	C(17)	2.80	H(23C)	H(31A)	2.49

b) Inter-molecular

		Symmetry Operation[a]				
Atom 1	Atom 2	R	x	y	z	Dist.
O(1)	H(25)	2	1	0	0	2.57
O(2)	H(20)	1	−1	0	0	2.52
H(2)	H(19)	4	1	−1	0	2.45
H(3)	H(23B)	4	0	0	0	2.55
H(4)	H(25)	1	0	1	0	2.65
H(11)	H(27)	3	0	−1	0	2.01
H(21)	H(30C)	3	0	0	0	2.22
H(22)	H(31B)	4	1	−1	0	2.43
H(25)	H(31B)	4	1	−1	0	2.22

[a] The second atom has been moved by rotation and/or inversion operator (R) and by (x, y, z) unit cell translations prior to distance calculation. The rotation operators are:
1) x, y, z
2) −x, 1/2 + y, 1/2 − z
3) 1/2 − x, −y, 1/2 + z
4) 1/2 + x, 1/2 − y, z

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TABLE XXIII. Comparison of Cp–Ph Interactions in Mo–Benzamidines.

$Cp(CO)_2MoN(R)C(Ph)N(R')$ R	R′	Space Group	Interaction[a] Type	Inter-Planar Angle (°)	Centroid–Centroid Dist. (Å)	Shortest C...H Contact (Å)
CH_2Ph (BENZ-I)	S-CHMePh	P1	Cp–Ph(II)	58.8	4.60	2.73
			Cp–Ph(III)	62.6	4.52	2.78
			Cp–Ph(II)	59.4	4.86	3.25
			Cp–Ph(III)	56.0	4.62	2.91
CH_2Ph (BENZ-II)	S-CHMePh	$P2_12_12_1$	Cp–Ph(II)	52.8	4.82	2.95
S-CHMePh (BENZ-III)	S-CHMePh	$P2_12_12_1$	Cp–Ph(II)	52.3	4.73	2.90
S-CHMePh (BENZ-IV)	S-CHMePh	$P2_12_12_1$	Cp–Ph(II)	53.0	4.67	2.80

[a] Ph(II) and Ph(III) represent phenyl groups C(16)–C(21) and C(24)–C(29), respectively.

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