Références

ALCOCK, N. W., DE MEESTER, P. & KEMP, T. J. (1978). *Acta Cryst.* B**34**, 3367–3369.
BOK, L. D. C., LEIPOLDT, J. G. & BASSON, S. S. (1972). *Z. Anorg. Allg. Chem.* **389**, 307–314.
BROUTY, C. (1978). Thèse de Doctorat d'Etat, Univ. P. et M. Curie, Paris.
BROUTY, C., SPINAT, P. & WHULER, A. (1977). *Acta Cryst.* B**33**, 3453–3460.
BROUTY, C., SPINAT, P. & WHULER, A. (1979). *C. R. Acad. Sci.* **288**, 257–259.
BROUTY, C., SPINAT, P., WHULER, A. & HERPIN, P. (1976). *Acta Cryst.* B**32**, 2153–2159.
BROUTY, C., SPINAT, P., WHULER, A. & HERPIN, P. (1977). *Acta Cryst.* B**33**, 1913–1920.
BROUTY, C., WHULER, A., SPINAT, P. & HERPIN, P. (1977). *Acta Cryst.* B**33**, 2563–2572.
FRANK, F. C. & KASPER, J. S. (1959). *Acta Cryst.* **12**, 483–499.
HAUPT, H. J., HUBER, F. & PREUT, H. (1976). *Z. Anorg. Allg. Chem.* **422**, 255–260.
IWATA, M., NAKATSU, K. & SAITO, Y. (1969). *Acta Cryst.* B**25**, 2562–2571.
NAKATSU, K. (1962). *Bull. Chem. Soc. Jpn*, **35**, 832–839.
NAKATSU, K., SAITO, Y. & KUROYA, H. (1956). *Bull. Chem. Soc. Jpn*, **29**, 428–434.
NAKATSU, K., SHIRO, M., SAITO, Y. & KUROYA, H. (1957). *Bull. Chem. Soc. Jpn*, **30**, 158–164.
RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 1362–1372.
RAYMOND, K. N. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 2333–2338.
SPINAT, P., WHULER, A. & BROUTY, C. (1979*a*). *Acta Cryst.* B**35**, 2914–2922.
SPINAT, P., WHULER, A. & BROUTY, C. (1979*b*). *C. R. Acad. Sci.* **288**, 209–212.
TERBERG, J. (1939). *Recl Trav. Chim. Pays-Bas*, **58**, 93–98.
WHULER, A. (1978). Thèse de Doctorat d'Etat, Univ. P. et M. Curie, Paris.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1975). *Acta Cryst.* B**31**, 2069–2076.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1976*a*). *Acta Cryst.* B**32**, 2238–2239.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1976*b*). *Acta Cryst.* B**32**, 194–198.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1976*c*). *Acta Cryst.* B**32**, 2542–2544.
WHULER, A., BROUTY, C., SPINAT, P. & HERPIN, P. (1977). *Acta Cryst.* B**33**, 2877–2885.
WHULER, A., SPINAT, P. & BROUTY, C. (1980). En préparation.
WITIAK, D., CLARDY, J. C. & MARTIN, D. S. (1972). *Acta Cryst.* B**28**, 2694–2699.

Acta Cryst. (1980). B**36**, 551–556

Structures of Two Diastereomers of Tricarbonyl[5-ethyl-2-(5′-ethyl-1′,2′,3′,4′-tetrahydro-1′-methyl-2′-pyridyl)-1,6-dihydro-1-methylpyridine]chromium

BY JAMES TROTTER AND THOMAS C. W. MAK*

Department of Chemistry, The University of British Columbia, Vancouver, BC, Canada V6T 1W5

(*Received* 27 *June* 1979; *accepted* 6 *November* 1979)

Abstract

The structure and absolute configuration of two diastereomers of the title compound, $[Cr(C_{16}H_{26}N_2)(CO)_3]$, have been established by X-ray analysis. Isomer (I), a racemate composed of the configurations (2*S*, 2′*R*) and (2*R*, 2′*S*), is monoclinic, space group $C2/c$, with $a = 29{\cdot}537$ (2), $b = 11{\cdot}323$ (2), $c = 14{\cdot}594$ (2) Å, $\beta = 128{\cdot}55$ (1)°, $Z = 8$. Isomer (II), with enantiomeric components (2*S*, 2′*S*) and (2*R*, 2′*R*), is monoclinic, space group $P2_1/c$, with $a = 11{\cdot}430$ (2), $b = 10{\cdot}440$ (2), $c = 19{\cdot}566$ (2) Å, $\beta = 123{\cdot}43$ (1)°, $Z = 4$. The structures were determined from Mo $K\alpha$ diffractometer data by direct methods and refined to R 0·031 (I, 1801 observed reflections) and 0·035 (II, 2474 reflections). In both diastereomers the Cr atom is bonded to the envelope-like dihydropyridine ring through the lone pair and π electrons of the dienamine system to achieve a distorted octahedral coordination. Steric interaction between the dihydropyridine ligand and its tetrahydropyridine substituent is more severe in (II), and this accounts mainly for the different conformations of the tetrahydropyridine ring in the two diastereomers.

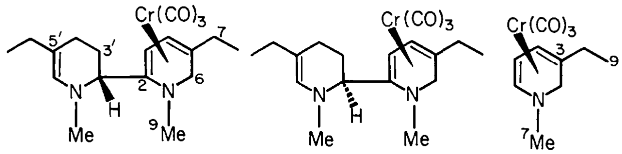
Introduction

It is now well established that dihydropyridines function as important intermediates in biological redox reactions (Eisner & Kuthan, 1972) and in certain areas of plant biosynthesis (Scott & Wei, 1972, and references cited therein). Electron-withdrawing groups

* On sabbatical leave from The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong.

0567-7408/80/030551-06$01.00

stabilize the dihydropyridine system, and very stable tricarbonylchromium complexes of the 3-ethyl-1-methyl- (III) (Bear, Cullen, Kutney, Ridaura, Trotter & Zanarotti, 1973), 5-ethyl-1-methyl- (V) (Bear *et al.*, 1973), 1,4-dimethyl- (VI) and other substituted (Fischer & Öfele, 1967; Öfele, 1968) 1,2-dihydropyridines have been synthesized. X-ray analyses of complexes (III) and (V) (Bear & Trotter, 1973) and (VI) (Huttner & Mills, 1972) showed that the dihydropyridine system serves as a pentahapto six-electron π donor.



(I) (II) (III)

The reaction of tricarbonyl(3-ethyl-1,2-dihydro-1-methylpyridine)chromium (III) with methyllithium gave a high yield of three isomeric products of molecular formula $C_{19}H_{26}CrN_2O_3$ (Kutney, Mak, Mostowicz, Trotter & Worth, 1979). The isomers displayed virtually identical IR, UV, PMR, and mass spectra, all of which indicate the substitution of a tetrahydropyridyl group into the dihydropyridine ligand in the metal complex. In order to establish the structural assignments and to obtain precise information about the bonding and stereochemistry of these novel systems, all three isomers were subjected to X-ray analysis. Two of these, which turn out to be diastereomeric forms of the title compound, constitute the subject of the present report. As represented by structural formulae (I) and (II), they are differentiated by their chirality at C(2′). The third, a structural isomer (IV) differing from (I) only in the location of the double bond in the tetrahydropyridine ring, will be dealt with in the following paper (Trotter & Mak, 1980).

Experimental

Complexes (I) and (II) are respectively dark red and red in colour, both crystallizing as plates with (010) well developed. Unit-cell and space-group data were determined from film and diffractometer measurements.

Crystal data

(I), $C_{19}H_{26}CrN_2O_3$, $M_r = 382.44$, monoclinic, space group $C2/c$ (No. 15), $a = 29.537$ (2), $b = 11.323$ (2), $c = 14.594$ (2) Å, $\beta = 128.55$ (1)°, $V = 3817.2$ Å^3, $D_c = 1.331$ Mg m^{-3} for $Z = 8$, μ(Mo $K\alpha$) = 0.638 mm^{-1}.

(II), $C_{19}H_{26}CrN_2O_3$, $M_r = 382.44$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.430$ (2), $b = 10.440$ (2), $c = 19.566$ (2) Å, $\beta = 123.43$ (1)°, $V = 1948.4$ Å^3, $D_c = 1.303$ Mg m^{-3} for $Z = 4$, μ(Mo $K\alpha$) = 0.625 mm^{-1}.

Crystal samples of approximate size $0.3 \times 0.1 \times 0.3$ mm were used in data collection for both complexes. Intensities were recorded, to $\theta = 26$ and 27.5° for (I) and (II) respectively, with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD-4 diffractometer. A variable-speed ω–2θ scan over a range of $r = (0.85 + 0.35 \tan \theta)$° in ω was employed. The scan was extended at both ends by $r/4$ for background measurement. Crystal orientation was monitored every 100 reflections and the intensities of three standard reflections were checked hourly throughout the data collection. Of the 3738 (I) and 4472 (II) independent reflections recorded, 1801 (I, 48.2%) and 2474 (II, 55.3%) had intensities greater than $3\sigma(I)$ above background where $\sigma^2(I) = S + B + (0.04S)^2$, with S = scan count and B = normalized background count. The remaining reflections in both compounds were classified as unobserved. Check-reflection scaling and Lorentz and polarization factors were applied to the data but no absorption correction was made (maximum possible error in $F \sim 3\%$).

Both structures were solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). In each case the initial E map revealed most of the non-hydrogen atoms, and the remaining ones were located from subsequent electron-density maps. After anisotropic refinement of all 25 non-hydrogen atoms in the asymmetric unit, difference Fourier syntheses were computed which gave the positions of all 26 H atoms. The latter were assigned estimated isotropic thermal parameters commensurately larger than those of the atoms to which they are bonded and were included, but not refined, in the final stage of refinement. For (I) convergence was reached at $R = 0.031$, weighted $R = 0.038$, for 1801 observed reflections. The corresponding values for (II) are 0.035 and 0.048 respectively for 2474 observed data. The final difference maps were essentially flat.

Scattering factors for C, N, O, and Cr atoms were generated from the analytical expressions of Cromer & Mann (1968), and those for H were from Stewart, Davidson & Simpson (1965). Computations were performed on an Amdahl 470 system with a highly modified version of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$.

A common atom numbering for both molecules is adopted; *ORTEP* (Johnson, 1965) plots of (I) and (II) are shown in Fig. 1(*a*) and (*b*) respectively. The final positional parameters are listed in Table 1.* Bond

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34861 (77 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2 HU, England.

Table 1. *Fractional coordinates* (Cr $\times 10^5$; C, N, *and* O $\times 10^4$; H $\times 10^3$) *with e.s.d.'s in parentheses*

	(I)			(II)		
	x	*y*	*z*	*x*	*y*	*z*
Cr	15378 (2)	−7311 (4)	12902 (4)	22873 (3)	19303 (3)	35928 (2)
N(1)	1244 (1)	548 (2)	−25 (2)	2200 (2)	2007 (2)	2480 (1)
C(2)	1414 (1)	1159 (2)	994 (2)	3523 (2)	2498 (2)	3100 (1)
C(3)	1983 (1)	983 (2)	1984 (2)	4344 (2)	1701 (2)	3760 (1)
C(4)	2349 (1)	192 (3)	1957 (2)	3847 (2)	473 (2)	3803 (1)
C(5)	2179 (1)	−249 (3)	917 (3)	2624 (2)	−12 (2)	3147 (1)
C(6)	1696 (1)	396 (3)	−167 (2)	2108 (2)	606 (2)	2335 (1)
C(7)	2549 (1)	−1067 (3)	822 (3)	2026 (3)	−1297 (2)	3146 (1)
C(8)	2864 (2)	−407 (3)	453 (3)	2593 (3)	−1873 (3)	3983 (2)
C(9)	650 (1)	638 (3)	−1128 (2)	1258 (2)	2772 (2)	1739 (1)
N(1′)	1234 (1)	3242 (2)	1059 (2)	5109 (2)	4331 (2)	3782 (1)
C(2′)	1020 (1)	2043 (2)	974 (2)	4052 (2)	3765 (2)	2988 (1)
C(3′)	995 (1)	1866 (3)	1980 (3)	4654 (3)	3536 (3)	2467 (2)
C(4′)	572 (1)	2734 (3)	1875 (3)	5983 (3)	2754 (3)	2933 (2)
C(5′)	676 (1)	3957 (3)	1656 (3)	6988 (3)	3299 (3)	3766 (2)
C(6′)	977 (1)	4137 (3)	1274 (2)	6504 (3)	4057 (3)	4094 (2)
C(7′)	428 (2)	4943 (3)	1913 (3)	8520 (3)	2938 (3)	4212 (2)
C(8′)	532 (2)	6174 (3)	1722 (3)	8808 (5)	1528 (4)	4444 (3)
C(9′)	1256 (1)	3543 (3)	110 (3)	4757 (3)	5514 (3)	3993 (2)
O(1)	2132 (1)	−2184 (2)	3465 (2)	3038 (2)	1646 (2)	5309 (1)
C(10)	1911 (1)	−1599 (3)	2633 (3)	2765 (3)	1737 (2)	4646 (2)
O(2)	489 (1)	−1077 (2)	1127 (3)	1491 (2)	4561 (2)	3807 (1)
C(11)	892 (1)	−924 (3)	1170 (3)	1802 (2)	3566 (3)	3695 (1)
O(3)	1249 (1)	−2999 (3)	−4 (3)	−600 (2)	949 (2)	2941 (1)
C(12)	1357 (1)	−2107 (3)	475 (3)	502 (3)	1350 (2)	3193 (1)
H(3)	214	143	272	531	198	422
H(4)	274	−5	272	438	−4	433
H(6*a*)	183	119	−23	272	34	213
H(6*b*)	155	−6	−90	112	34	192
H(7*a*)	284	−149	159	98	−120	286
H(7*b*)	229	−171	21	221	−190	282
H(8*a*)	312	−96	43	212	−271	393
H(8*b*)	258	−5	−35	364	−205	427
H(8*c*)	311	24	103	245	−127	433
H(9*a*)	60	141	−152	124	368	190
H(9*b*)	57	−2	−167	162	276	137
H(9*c*)	37	60	−96	30	241	144
H(2′)	61	196	20	324	437	269
H(3′*a*)	88	103	199	394	310	195
H(3′*b*)	139	200	275	487	440	232
H(4′*a*)	16	249	119	573	186	299
H(4′*b*)	60	272	261	644	273	262
H(6′)	102	499	112	722	450	463
H(7′*a*)	0	481	141	890	319	386
H(7′*b*)	59	487	276	908	347	473
H(8′*a*)	96	633	221	850	127	481
H(8′*b*)	36	629	87	825	97	392
H(8′*c*)	36	677	193	982	129	470
H(9′*a*)	139	438	18	541	568	459
H(9′*b*)	152	300	11	478	623	367
H(9′*c*)	86	346	−69	376	545	387

distances and angles are given in Table 2. Torsion angles in the organic ligand are given in Table 3.

Discussion

Substituted (π-arene)chromium tricarbonyls lacking a plane of symmetry [*e.g.* formula (III)] may exist as enantiomeric pairs. The preparation and resolution of chiral metallocenes has been reviewed (Schlögl, 1965, 1970). The title compound is of interest in view of the incorporation of additional skeletal chirality in one of the substituents. As illustrated in Fig. 1, diastereomers (I) and (II) differ mainly in the configuration of the second chiral centre at C(2′). In accordance with the recommended nomenclature for metallocene chirality (Cahn, Ingold & Prelog, 1966; IUPAC, 1970), (I) and (II), as represented by their structural formulae and in Fig. 1, are designated (2*S*,2′*R*) and (2*S*,2′*S*) respec-

Table 2. *Molecular dimensions*

(*a*) Bond distances (Å)

	(I) (σ = 0·003–0·004 for Cr–C,N; 0·004–0·005 for others)	(II) (σ = 0·002–0·003 for Cr–C,N; 0·003–0·005 for others)	(III) (σ = 0·005–0·008 for Cr–C,N; 0·007–0·010 for others)
Cr–N(1)	2·111	2·126	2·136
Cr–C(2)	2·168	2·185	2·175
Cr–C(3)	2·205	2·201	2·205
Cr–C(4)	2·208	2·204	2·202
Cr–C(5)	2·338	2·322	2·310
Cr–C(10)	1·825	1·830	1·837
Cr–C(11)	1·816	1·840	1·838
Cr–C(12)	1·827	1·840	1·835
O(1)–C(10)	1·162	1·159	1·169
O(2)–C(11)	1·165	1·158	1·142
O(3)–C(12)	1·155	1·149	1·158
N(1)–C(2)	1·419	1·414	1·401
N(1)–C(6)	1·483	1·483	1·479
N(1)–C(9)	1·470	1·476	1·468
C(2)–C(3)	1·388	1·380	1·364
C(3)–C(4)	1·423	1·423	1·446
C(4)–C(5)	1·361	1·372	1·376
C(5)–C(6)	1·502	1·501	1·514
C(5)–C(7)	1·506	1·505	1·528
C(7)–C(8)	1·528	1·514	1·525
C(2)–C(2′)	1·522	1·520	
N(1′)–C(2′)	1·470	1·467	
N(1′)–C(6′)	1·415	1·388	
N(1′)–C(9′)	1·467	1·429	
C(2′)–C(3′)	1·530	1·531	
C(3′)–C(4′)	1·520	1·510	
C(4′)–C(5′)	1·496	1·496	
C(5′)–C(6′)	1·326	1·317	
C(5′)–C(7′)	1·505	1·512	
C(7′)–C(8′)	1·491	1·522	
Cr···C(6)	2·759	2·717	2·750

(*b*) Bond angles (°)

	(I) (σ = 0·1 at Cr; 0·3–0·4 for others)	(II) (σ = 0·1 at Cr; 0·2–0·3 for others)	(III) (σ = 0·3 at Cr; 0·5–0·7 for others)
C(10)–Cr–C(11)	86·2	84·3	87·6
C(10)–Cr–C(12)	88·7	90·9	89·1
C(11)–Cr–C(12)	88·4	91·2	91·9
Cr–C(10)–O(1)	177·4	177·8	178·1
Cr–C(11)–O(2)	177·5	174·8	177·1
Cr–C(12)–O(3)	177·4	177·8	178·0
C(2)–N(1)–C(6)	116·3	116·8	117·1
C(2)–N(1)–C(9)	121·0	120·2	117·1
C(6)–N(1)–C(9)	114·8	114·2	114·7
N(1)–C(2)–C(3)	115·4	116·0	118·3
N(1)–C(2)–C(2′)	122·3	120·9	
C(2′)–C(2)–C(3)	122·0	122·7	
C(2)–C(3)–C(4)	120·6	120·7	119·3
C(3)–C(4)–C(5)	120·2	120·8	119·7
C(4)–C(5)–C(6)	116·4	115·8	117·1
C(4)–C(5)–C(7)	122·9	123·9	124·2
C(6)–C(5)–C(7)	118·0	118·0	116·5
C(5)–C(7)–C(8)	111·6	115·5	115·0
N(1)–C(6)–C(5)	104·7	106·1	104·6
C(2′)–N(1′)–C(6′)	114·7	117·3	
C(2′)–N(1′)–C(9′)	113·9	117·1	
C(6′)–N(1′)–C(9′)	112·9	119·3	
N(1′)–C(2′)–C(3′)	108·4	111·0	
N(1′)–C(2′)–C(2)	108·8	111·0	
C(2)–C(2′)–C(3′)	112·9	108·7	
C(2′)–C(3′)–C(4′)	110·3	110·7	
C(3′)–C(4′)–C(5′)	110·8	111·5	
C(4′)–C(5′)–C(6′)	120·8	118·9	
C(4′)–C(5′)–C(7′)	115·9	119·0	
C(6′)–C(5′)–C(7′)	123·3	122·2	
C(5′)–C(7′)–C(8′)	117·3	113·8	
N(1′)–C(6′)–C(5′)	125·3	126·8	

Notes: Atom numbering in the substituted dihydropyridine ligand of complex (III) (Bear & Trotter, 1973) is different from that for (I) and (II) (see structural formulae). In Tables 2, 3 the atoms of (III) are re-labelled to correspond to those of (I) and (II) for ready comparison of chemically equivalent distances and angles. In Bear & Trotter (1973), *y* for C(11) and the Cr–C(12)–O(12) angle are misprinted; correct values are 0·2589 and 177·1, respectively.

tively. It should be noted that, since both diastereomers crystallize in centrosymmetric space groups, the above configurations are paired up with an equal number of enantiomorphs, namely (2*R*,2′*S*) and (2*R*,2′*R*) respectively, in their optically inactive crystal forms.

The structural data of tricarbonyl(3-ethyl-1,2-dihydro-1-methylpyridine)chromium (III) (Bear & Trotter, 1973), considered as the parent compound of (I) and (II), are also given in Table 2 for ready comparison of chemically equivalent distances and angles in all three complexes. In each instance the dihydropyridine ligand is attached to the Cr atom in an η^5 fashion through the N(1) lone pair and the π electrons of the diene system. The distances of the metal atom to the centres of the C(2)–C(3) and C(4)–C(5) double bonds are, respectively, for (I): 2·074 and 2·170; for (II): 2·082 and 2·157; and for (III): 2·082 and 2·149 Å. The distances from Cr to N(1) and C(2)–C(5) of the dienamine system are all shorter than Cr–C(arene) distances in the range 2·20–2·25 Å found in numerous (π-arene)chromium tricarbonyl compounds (Sneeden, 1975). In the $Cr(CO)_3$ group, the measured dimensions (Table 2) support the observation (Brown, 1978) that, for Cr–C–O groups *trans* to a π-bonded ring, Cr–C = 1·84, C–O = 1·15 Å and the Cr–C–O angle centres around 178°. The OC–Cr–CO angles, ranging from 84·3 to 91·9°, seem to be more sensitive

Table 3. *Torsion angles* (°)

The sign convention is that defined by Klyne & Prelog (1960).

	(I) (σ = 0·3–0·4)	(II) (σ = 0·2–0·3)	(III)* (σ = 0·5–0·7)
C(9)–N(1)–C(2)–C(3)	178·9	−178·4	−176·0
N(1)–C(2)–C(3)–C(4)	−3·0	−1·2	−1·3
C(2)–C(3)–C(4)–C(5)	11·1	8·4	8·1
C(3)–C(4)–C(5)–C(6)	17·5	18·2	18·9
C(3)–C(4)–C(5)–C(7)	178·6	−179·6	−178·9
C(4)–C(5)–C(6)–N(1)	−48·6	−46·8	−47·1
C(4)–C(5)–C(7)–C(8)	−99·6	17·8	29·0
C(8)–C(7)–C(5)–C(6)	61·2	179·7	−168·7
C(7)–C(5)–C(6)–N(1)	149·3	149·9	149·3
C(5)–C(6)–N(1)–C(9)	−153·0	−157·0	−161·3
C(5)–C(6)–N(1)–C(2)	57·7	55·3	54·8
C(6)–N(1)–C(2)–C(3)	−33·8	−32·8	−33·1
C(6)–N(1)–C(2)–C(2′)	140·1	140·6	
C(9)–N(1)–C(2)–C(2′)	−7·2	−5·1	
N(1)–C(2)–C(2′)–C(3′)	133·7	−80·6	
N(1)–C(2)–C(2′)–N(1′)	−105·9	157·1	
C(2)–C(2′)–C(3′)–C(4′)	−177·2	−68·6	
C(2′)–C(3′)–C(4′)–C(5′)	−47·7	−50·1	
C(3′)–C(4′)–C(5′)–C(6′)	17·8	21·1	
C(3′)–C(4′)–C(5′)–C(7′)	−161·2	−160·2	
C(4′)–C(5′)–C(7′)–C(8′)	179·0	−65·8	
C(8′)–C(7′)–C(5′)–C(6′)	0·1	112·8	
C(7′)–C(5′)–C(6′)–N(1′)	177·7	−172·1	
C(4′)–C(5′)–C(6′)–N(1′)	−1·2	6·5	
C(5′)–C(6′)–N(1′)–C(9′)	148·7	−154·0	
C(5′)–C(6′)–N(1′)–C(2′)	16·1	−2·7	
C(6′)–N(1′)–C(2′)–C(2)	−168·5	93·1	
C(6′)–N(1′)–C(2′)–C(3′)	−45·4	−27·9	
C(9′)–N(1′)–C(2′)–C(2)	59·3	−114·9	
C(9′)–N(1′)–C(2′)–C(3′)	−177·5	124·1	
N(1′)–C(2′)–C(2)–C(3)	67·6	−30·1	
N(1′)–C(2′)–C(3′)–C(4′)	62·2	53·7	
C(2′)–C(2)–C(3)–C(4)	−176·9	−174·4	
C(3)–C(2)–C(2′)–C(3′)	−52·7	92·3	

* See notes in Table 2. Note that the reported atomic coordinates for (III) (Bear & Trotter, 1973) correspond to the opposite enantiomorph.

Table 4. *Least-squares planes and deviations* ($\times 10^3$ Å, $\sigma \sim 0{\cdot}003$ Å) *of selected atoms from the planes*

Planes are defined in terms of Cartesian coordinates by $AX + BY + CZ = D$; X and Y are parallel to **a** and **b** respectively, and Z is parallel to **c***.

(*a*) Plane 1: N(1) – C(5) in the dihydropyridine ring

Compound	*A*	*B*	*C*	*D*
(I)	0·5479	0·8032	−0·2338	2·5511
(II)	0·8167	−0·3592	−0·4517	−2·6840

	N(1)	C(2)	C(3)	C(4)	C(5)	C(6)
(I)	−20	31	34	−73	48	682
(II)	−27	20	18	−55	47	647

(*b*) Plane 2: C(4′) – C(7′) in the tetrahydropyridine ring

Compound	*A*	*B*	*C*	*D*
(I)	−0·3306	−0·0447	−0·9427	−2·1488
(II)	0·4592	0·7894	−0·4075	2·0096

	N(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)	C(9′)	C(2)
(I)	−42	294	−452	−2	5	−2	−2	658	−62
(II)	−148	−247	485	−3	7	−2	−3	399	−1699

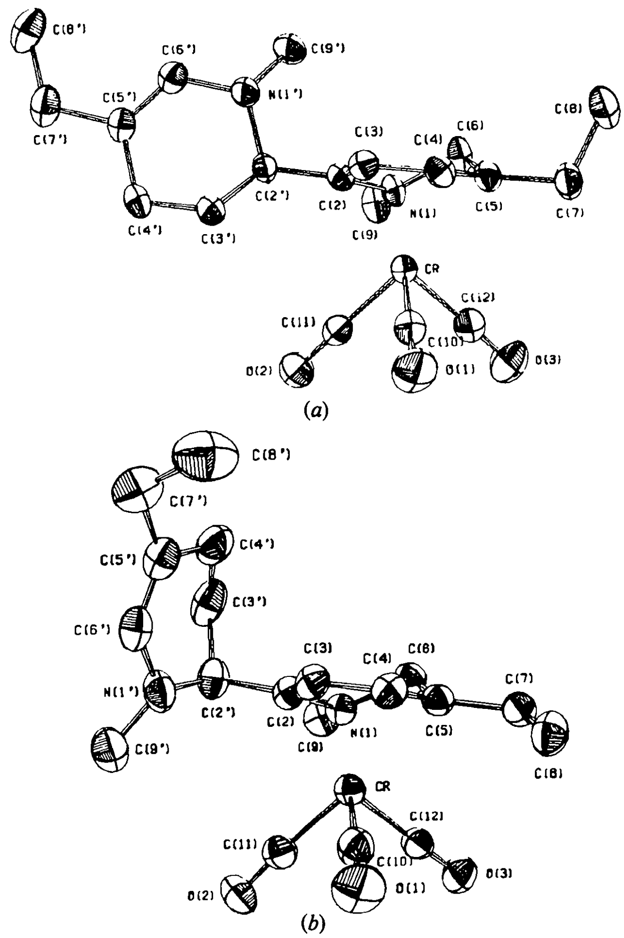


Fig. 1. Atom numbering and stereochemical relationships of the diastereomers, each viewed from the same perspective relative to its chromium tricarbonyl group. The thermal ellipsoids are drawn at the 40% probability level, and H atoms have been omitted for the sake of clarity. (*a*) Isomer (I) with the (2*S*,2′*R*) configuration. (*b*) Isomer (II) with the (2*S*,2′*S*) configuration.

to the nature of the substituents in the π ligand and the mode of molecular packing. The orientation of the $Cr(CO)_3$ group with respect to the dihydropyridine ring is such that a distorted octahedral coordination results for the Cr atom.

The bond-length variation in the dihydropyridine ring reflects the conjugated nature of the dienamine system. The measured bond angles around N(1) imply that its hybridization is very close to sp^2 in (I) and (II) and has a higher p content in (III). The torsion angles (Table 3) and the deviations of atoms from the least-squares plane through the system N(1) – C(5) (Table 4) show that the heterocyclic ring, which adopts an envelope conformation, is puckered in virtually the same way in all three complexes. The dispositions of the ethyl groups are, however, different, with the terminal C(8) atom on the same side of the ring as the $Cr(CO)_3$ group for (II) and (III), and on the opposite side for (I).

In diastereomers (I) and (II), the position of the double bond in each tetrahydropyridine ring is established by the observed C—C bond lengths and direct location of the H atoms. Unlike the dihydropyridine rings, the tetrahydropyridine rings assume very different conformations, as can be seen from the torsion angles (Table 3) and atom displacements from the least-squares plane through C(4′) – C(7′) (Table 4). Conjugation in the enamine systems of both diastereomers is clearly shown by the significantly shorter N(1′)—C(6′) bonds as compared with the N(1′)—C(2′) bonds. In contrast to the virtually planar arrangement of bonds around N(1), the configuration at N(1′) is distinctly pyramidal. The mean C—N(1′)—C angles of 113·8° (r.m.s. deviation from mean, 0·7°) in (I) and 117·9° (r.m.s. deviation, 1·0°) in (II) are both larger than the corresponding value of 111·1° for an *N*-methylpiperidine moiety (Ruble, Hite & Soares, 1976), in accord with the picture of delocalization of the N(1′) lone pair. The significant difference in mean C—N(1′)—C angles implies more *p* character in the hybridization of N(1′) in (I) than in (II). In substantiation of this, the N(1′)—C bonds in (I) are longer than those in (II).

The principal difference in the two diastereomers is that the tetrahydropyridine ring, as a substituent, interacts much more strongly with the dihydropyridine ligand in (II) (Fig. 1). The finer structural details, in particular the different tetrahydropyridine ring conformations, are explicable in terms of ligand–substituent steric repulsions. For each diastereomer, the crystal structure is composed of a packing of well separated molecules, the shortest intermolecular contacts corresponding to normal van der Waals interactions.

The authors acknowledge financial support by the Natural Sciences and Engineering Research Council Canada, and thank Drs J. P. Kutney and D. Mostowicz for the crystal samples, and the University of British Columbia Computing Centre for assistance.

References

BEAR, C. A., CULLEN, W. R., KUTNEY, J. P., RIDAURA, V. E., TROTTER, J. & ZANAROTTI, A. (1973). *J. Am. Chem. Soc.* **95**, 3058–3060.

BEAR, C. A. & TROTTER, J. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2285–2288.

BROWN, I. D. (1978). *Coord. Chem. Rev.* **26**, 161–206.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

CAHN, R. S., INGOLD, C. K & PRELOG, V. (1966). *Angew. Chem. Int. Ed. Engl.* **5**, 385–415.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

EISNER, U. & KUTHAN, J. (1972). *Chem. Rev.* **72**, 1–42.

FISCHER, E. O. & ÖFELE, K. (1967). *J. Organomet. Chem.* **8**, P5–P6.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HUTTNER, G. & MILLS, O. S. (1972). *Chem. Ber.* **105**, 3924–3935.

IUPAC (1970). *J. Org. Chem.* **35**, 2849–2867.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.

KUTNEY, J. P., MAK, T. C. W., MOSTOWICZ, D., TROTTER, J. & WORTH, B. R. (1979). Submitted for publication.

ÖFELE, K. (1968). *Angew. Chem. Int. Ed. Engl.* **6**, 988–989.

RUBLE, J. R., HITE, G. & SOARES, J. R. (1976). *Acta Cryst.* B**32**, 136–140.

SCHLÖGL, K. (1965). *Topics in Stereochemistry*, Vol. 1, edited by N. L. ALLINGER & E. L. ELIEL, pp. 39–91. New York: Wiley–Interscience.

SCHLÖGL, K. (1970). *Pure Appl. Chem.* **23**, 413–432.

SCOTT, A. I. & WEI, C. C. (1972). *J. Am. Chem. Soc.* **94**, 8262–8267.

SNEEDEN, R. P. A. (1975). *Organochromium Compounds*, pp. 115–122. New York: Academic Press.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TROTTER, J. & MAK, T. C. W. (1980). *Acta Cryst.* B**36**, 557–560.