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CONFORMATIONAL AND CONFIGURATIONAL CHIRALITY OF 1,2-DIMETHYLAMINOALKYLFORMYLCYMANTRENES. MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF $(-)_{578}$-1-[α-(N,N-DIMETHYLAMINO)ETHYL]-2-FORMYLCYMANTRENE

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Summary

The molecular structure and the absolute configuration of $(-)_{578}$-1-[α-(N,N-dimethylamino)ethyl]-2-formylcymantrene have been established by the X-ray method. These data were used for the direct determination of the orientation and stereochemistry of the preferable attack of n-BuLi on metallation of [α-(N,N-dimethylamino)ethyl]cymantrene. CD and UV spectra of $(-)$-(S)-1-[(R)-α-(N,N-dimethylamino)ethyl]-2-formylcymantrene (planar and central chirality) and $(-)$-(S)-1-N,N-dimethylaminomethyl-2-formylcymantrene, I (only planar chirality) and related compounds have been studied, a change in both the sign and the intensity of Cotton effects is observed between solutions of I and II in aprotic solvents and solutions in 0.1 N HCl and quaternary salts of these compounds. The data obtained indicate that the optical characteristics of aminoaldehydes of cymantrene are determined by the conformation of these molecules but not by their absolute configuration.

Introduction

The absolute (S)-planar (metallocene) configuration of $(-)_{578}$-1-(N,N-dimethylaminomethyl)-2-formylcymantrene (I) has been recently [1] established by an X-ray analysis.

In this paper the X-ray analysis of the molecular structure and absolute configuration of $(-)_{578}$-1-[α-(N,N-dimethylamino)ethyl]-2-formylcymantrene (II) are given; in addition to the planar chirality, this molecule also has a chiral center in the amino substituent. Therefore, knowledge of the absolute configuration of the $(-)$-enantiomers of I and II makes it possible to consider the effect of different elements of chirality on the optical properties of these compounds.

Aminoaldehyde $(-)$-II is the predominant isomer among the three aminoformyl

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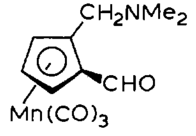
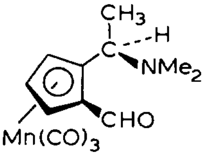
derivatives of cymantrene obtained in metallation of (+)-[α-(*N,N*-dimethylamino)ethyl]-cymantrene (III) followed by treating the resulting organolithium compounds with dimethylformamide [2,3]. Consequently, the determination of the molecular structure and absolute configuration of (−)-II provides direct evidence for the orientation and stereochemistry of the preferred attack of n-BuLi in the metallation of III.



(−)-(*S*)-I



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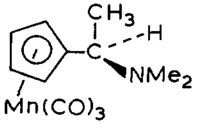
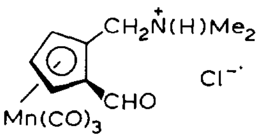
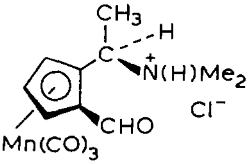


(+)-(*R*)-III



(+)-(*S*)-VIII



(+)-(*R,S*)-VIII

Results and discussion

I. Molecular structure and absolute configuration of $(-)_{578}$*-II*

The sample of (−)-II employed for X-ray analysis was obtained by the procedure described previously [3]; diastereomeric purity of the compound was verified from the PMR (360 MHz) data [3].

The molecular structure of (−)-II in the true absolute configuration and bond lengths are shown in Fig. 1. The coordinates of non-hydrogen atoms and parameters of temperature factors are given in Table 1; values of bond angles are presented in Table 2. The Mn atom in molecule II has the usual "piano-stool" coordination characteristic of monocyclopentadienyl complexes $(\eta^5\text{-}C_5H_5)ML_3$ (L is a monodentate two-electron donor) with a substantially undistorted C_{3v} symmetry of the $Mn(CO)_3$ fragment, the values of bond angles (O)C–Mn–C(O) being within the range of 91.3–92.4°. The cyclopentadienyl ring is planar within ±0.001 Å. The atoms C(9) and C(10) of the substituents are not strictly within the ring plane, but are displaced from it in opposite sides by 0.073(2) and 0.146(3) Å, respectively, the asymmetric atom C(10) being turned aside from the metal atom. A similar pattern is observed in a molecule of (−)-(*S*)-I [1], wherein the carbon atom of the CHO group and the methylene carbon atom of the $CH_2N(CH_3)_2$ group are displaced from the plane of the cyclopentadienyl ligand by 0.077 and 0.163 Å, respectively in the same directions as the atoms C(9) and C(10) in the molecule of (−)-II. The displacement of the methine carbon atom of the CH(Me)NCOMe group from the ring plane by 0.10 Å is also observed in the molecule of (+)-(*R*)-[α-(*N*-acetylamino)ethyl]-cymantrene (IV) [4]. The aldehyde group in II forms a dihedral angle of 10.4° with the cyclopentadienyl ring (in I this angle is 6.9°), whereas the fragment C(5)C(10)N is almost perpendicular to the ring plane (the angle is 94.1°).

The mean interatomic Mn-C(Cp) distances of 2.146(3) Å and C–C in the Cp ring of 1.427(3) Å are close to mean lengths of the same bonds found in the molecules of

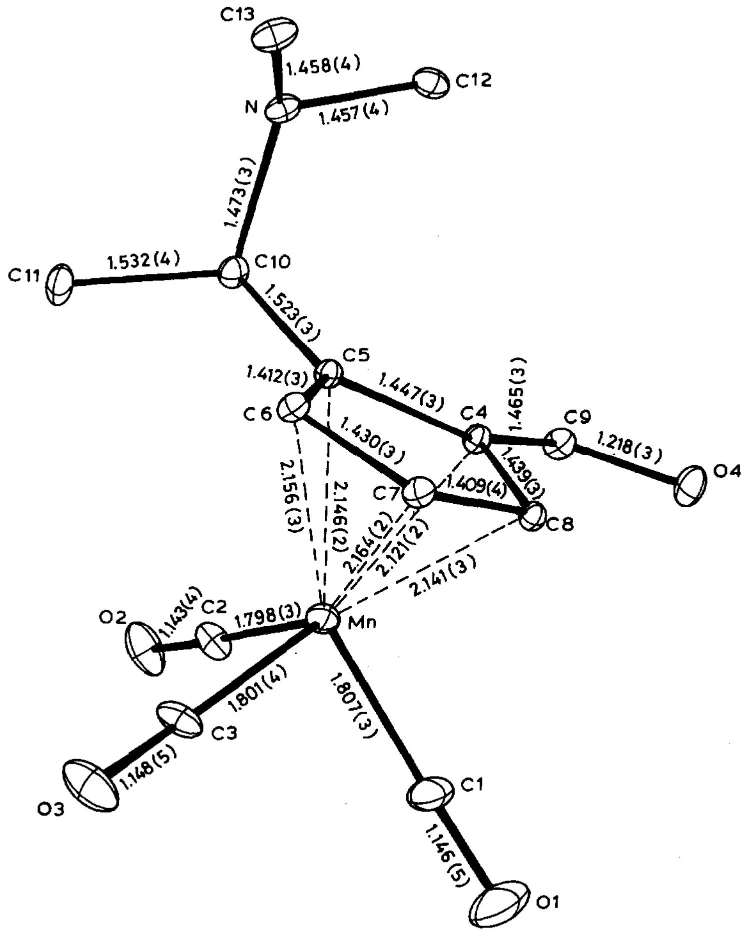


Fig. 1. The molecular structure of (+)-(*R*,*S*)-II.

cymantrene [5] and compounds I and IV. The geometrical parameters of the formyl and α-dimethylaminoethyl groups in II are quite normal and differ insignificantly from standard values for these kinds of bonds [6]: C(4)–C(9) 1.465(3), C(9)–O(4) 1.218(3) (in I 1.44 and 1.20 Å, respectively), C(10)–C(11) 1.532(4), C(10)–C(5) 1.523(3) and mean N–C(sp^3) of 1.465(4) Å. The coordination of the nitrogen atom is a distorted trigonal-pyramidal (or rather tetrahedral if judged by values of the bond angles C–N–C) with a lone electron pair occupying the fourth coordination place. The metal-carbonyl groups are linear with normal lengths of Mn–C (mean 1.803(4) Å) and C–O bonds (mean 1.146(5) Å).

Comparison of structural parameters of (−)-I (planar chirality) and (−)-II (central and planar chirality) shows that the presence of a methyl radical in the amino substituent of the molecule II results in only insignificant geometrical changes relative to the structure of I.

From Fig. 1 it follows that the asymmetric atom C(10) in (−)-II has the *R* configuration, while the planar chirality of the molecule correspond to the *S* configuration according to the reported nomenclature [7].

TABLE 1

ATOMIC COORDINATES ($\times 10^4$, FOR Mn$\times 10^5$) AND THEIR ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	14761(5)	15313(5)	10457(1)	1.46(1)	1.22(1)	1.46(1)	−0.03(1)	−0.13(1)	0.255(9)
O(1)	−1801(4)	3565(5)	1272(2)	2.6(1)	5.2(2)	7.7(2)	1.8(1)	−1.0(1)	−2.4(2)
O(2)	−594(4)	−1328(4)	554(1)	3.7(1)	3.4(1)	2.12(8)	−1.33(9)	−0.70(8)	−0.32(7)
O(3)	2045(5)	3238(5)	−11(1)	4.7(1)	5.9(2)	3.0(1)	−1.6(1)	−0.8(1)	2.6(1)
O(4)	18(3)	202(3)	2508(1)	2.25(7)	1.78(7)	2.22(7)	−0.06(6)	1.01(6)	0.03(6)
N	4816(3)	−3123(3)	1632(1)	1.56(7)	0.98(6)	2.27(8)	0.13(5)	0.02(6)	−0.06(6)
C(1)	−530(4)	2783(5)	1177(2)	1.90(9)	2.7(1)	3.9(2)	0.58(9)	−0.6(1)	−0.6(1)
C(2)	190(4)	−194(4)	740(1)	2.11(9)	2.32(9)	1.53(8)	−0.42(8)	−0.31(7)	0.26(7)
C(3)	1823(5)	2582(5)	401(1)	2.7(1)	3.1(1)	2.6(1)	−0.6(1)	−0.66(9)	1.3(1)
C(4)	2149(3)	402(3)	1803(1)	1.36(7)	0.91(6)	1.35(7)	−0.04(6)	0.14(6)	0.00(6)
C(5)	3292(3)	−339(3)	1389(1)	1.35(8)	0.96(6)	1.29(7)	−0.04(6)	0.08(6)	−0.09(5)
C(6)	4295(3)	1054(3)	1168(1)	1.37(7)	1.22(7)	1.63(8)	−0.04(6)	0.23(6)	0.15(6)
C(7)	3810(3)	2644(3)	1435(1)	1.60(8)	0.94(6)	1.76(8)	−0.17(6)	0.06(6)	0.18(6)
C(8)	2491(3)	2251(3)	1825(1)	1.63(7)	0.99(6)	1.53(7)	−0.02(7)	0.15(7)	−0.15(6)
C(9)	788(3)	−489(3)	2130(1)	1.44(7)	1.10(7)	1.92(8)	−0.11(6)	0.24(7)	0.14(6)
C(10)	3531(4)	−2273(3)	1263(1)	1.73(7)	0.93(6)	1.65(8)	−0.03(7)	0.00(8)	−0.23(6)
C(11)	4071(5)	−2591(4)	673(1)	3.5(1)	1.77(9)	1.81(9)	0.21(9)	0.60(9)	−0.56(7)
C(12)	4149(4)	−3300(3)	2183(1)	2.06(8)	1.40(8)	2.04(9)	0.00(8)	−0.26(7)	0.34(7)
C(13)	6621(4)	−2394(4)	1632(1)	1.55(9)	1.77(9)	3.7(1)	0.03(8)	0.20(9)	0.12(9)

TABLE 2

VALUES OF BOND ANGLES

Bond angle	Value (°)	Bond angle	Value (°)
C(1)MnC(2)	91.3(1)	C(8)C(4)C(9)	124.1(2)
C(1)MnC(3)	92.4(2)	C(4)C(5)C(6)	106.8(2)
C(2)MnC(3)	91.9(1)	C(4)C(5)C(10)	126.5(2)
C(10)NC(12)	113.3(2)	C(6)C(5)C(10)	126.3(2)
C(10)NC(13)	115.6(2)	C(5)C(6)C(7)	109.3(2)
C(12)NC(13)	110.5(2)	C(6)C(7)C(8)	108.1(2)
MnC(1)O(1)	178.5(4)	C(4)C(8)C(7)	107.9(2)
MnC(2)O(2)	177.8(3)	O(4)C(9)C(4)	123.1(2)
MnC(3)O(3)	179.4(3)	NC(10)C(5)	112.3(2)
C(5)C(4)C(8)	107.9(2)	NC(10)C(11)	110.3(2)
C(5)C(4)C(9)	127.9(2)	C(5)C(10)C(11)	112.3(2)

II. Configuration, conformation and optical properties

From the above, it follows that (−)-enantiomers of aminoformylcymantrene derivatives I and II have the same metallocenyl configuration. Furthermore, the formyl groups in both compounds occupy substantially the same conformation, wherein the formyl group oxygen atom is bent away from the amino substituent. Also similar appear to be the values of $[\alpha]_{578}$, and the pattern and parameters of CD and UV spectra of these compounds in aprotic solvents, e.g. hexane (Fig. 2, Table 3).

The absorption band in the CD and UV spectra with λ_{max} of about 340 nm is a characteristic metallocenyl band of cymantrene derivatives [4,8], while the band with λ_{max} of about 290 nm is, from its position and logε value, apparently associated with the π–π^* transition of a conjugated carbonyl chromophore *. Indeed, in the UV and CD spectra of (+)-III and (*N,N*-dimethylaminomethyl)cymantrene (V) only one absorption band is observed in the 280–400 nm range (about 340 nm), while the UV spectrum of formylcymantrene (VI) has two bands in this range: the metallocenyl * (342 nm) and the π–π^* transition band (288 nm, logε = 3.24). The above assignment is supported by the lower intensity of the band at 290 nm is UV spectra of I and VI for solutions in alcohol compared to hexane solutions, which is associated with the formation of a corresponding acetal. In contrast, the intensity variation of the band at ~ 340 nm on changing the solvent is less significant.

By comparing values of specific rotation of solutions of (−)-(*S*)-I and (−)-(*R,S*)-II in hexane, one comes to the conclusion that the presence of a chiral centre in the substituent of II does not determine the pattern and parameters of CD curves of optically active 1,2-aminoalkylformylcymantrenes. Nevertheless, on going from (−)-I to (−)-II a change in intensity of both Cotton effects is observed, the most sensitive being the band of the formyl chromophore and not the cymantrenyl one. Furthermore, the value of $[\theta]_{341}$ for (−)-II is 3.5 times greater than the value of

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* The band of the n–π^* transition of the carbonyl group is likely to be in the absorption region of the cymantrenyl chromophore and is not seen due to its low intensity.

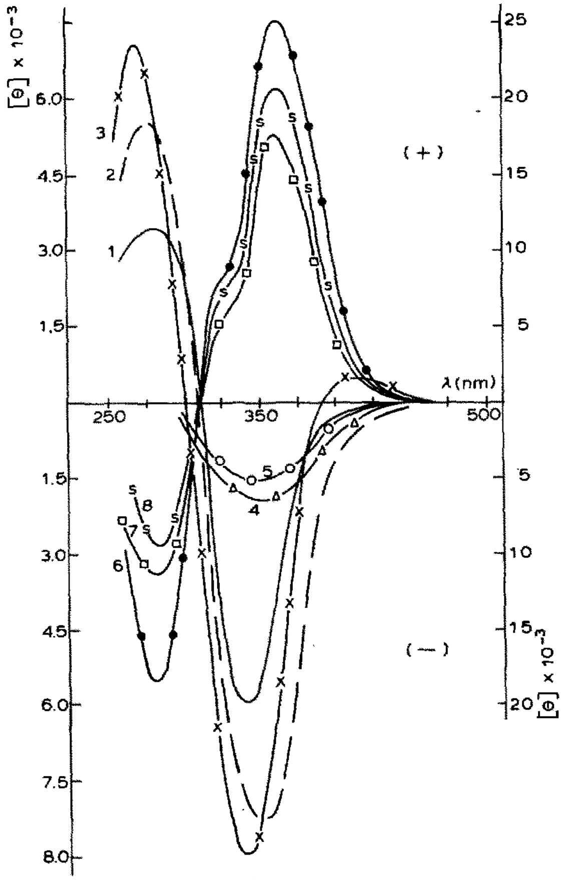

Fig. 2. CD spectra: left-hand scale 1. (*S*)-I in C_6H_{14}, 2. (*S*)-I in CH_3CN, 3. (*R*,*S*)-II in C_6H_{14}, 4. (*R*)-III in 0.1 *N* HCl, 5. (*R*)-III in CH_3CN; right-hand scale 6. (*R*,*S*)-VIII in 0.1 *N* HCl, 7. (*S*)-VII in 0.1 *N* HCl, 8. (S)-X in CH_3CN.

$[\theta]_{348}$ for the cymantrenyl chromophore in monosubstituted (+)-III [4].

It has been shown that a solution of (−)-(*S*)-I in 0.1 *N* HCl has a positive value of $[\alpha]_{436}$ [1]. A similar change of the sign of $[\alpha]$ in the range 436–578 nm is also observed in the case of (−)-(*R*,*S*)-II between solutions in aprotic solvents (hexane, CCl_4, $CHCl_3$) and a solution in 0.1 *N* HCl. Presumably, the change of the sign of $[\alpha]$ for protonated forms of aminoaldehydes of I and II (VII and VIII, respectively) is associated with the background effect which we have observed earlier in the case of (−)-(*R*)-(α-aminoethyl)-cymantrene and its derivatives [4]. However, the form of CD curves of (−)-(*S*)-VII and (+)-(*R*,*S*)-VIII (Fig. 2) shows that protonation of aminoaldehydes of I and II results in an significantly change in the dissymmetry of these molecules. In both cases protonation results in a sharp increase of intensity of Cotton effects and, more importantly, in the change of signs of these effects for both metallocenyl and carbonyl chromophores. Moreover, a bathochromic shift of the maximum of the metallocenyl Cotton effects by 22–25 nm and the appearance of a

TABLE 3

OPTICAL CHARACTERISTICS AND PARAMETERS OF UV SPECTRA OF THE OPTICALLY PURE COMPOUNDS

Compound	$[\alpha]_{578}/c$	CD spectrum $[\theta](°)/\lambda$(nm)	UV spectrum $\log\varepsilon/\lambda$(nm)	Solvent
(−)-(*S*)-I	−106.0/0.15	−6360/341	3.23/341	n-C_6H_{14}
		3670/285	3.37/288	
		−8350/350	3.28/345	CH_3CN
		5710/281	3.36/286	
		−1010/339	3.19/340	C_2H_5OH
		1785/303	3.18/288	
(−)-(*R*,*S*)-II	−147.1/0.04	−9160/339	3.22/340	n-C_6H_{14}
		7252/273	3.41/285	
(+)-(*R*)-III	10.8/0.14	−1840/348	3.04/331	n-C_6H_{14}
		−2000/345		0.1 *N* HCl
VI			3.12/342	n-C_6H_{14}
			3.24/288	
			3.13/342	C_2H_5OH
			3.15/286	
(+)-(*S*)-VII	418.0/0.122	18266/363	3.29/342	0.1 N HCl
		−12712/287	3.34/297	
(+)-(*R*,*S*)-VIII	556.4/0.135	25572/364	3.29/342	0.1 N HCl
		−18065/288	3.31/297	
(+)-IXa	3810[a]	−6484/582	2.12/620	C_2H_5OH
		41553/360	3.53/350[b]	
		−2970/295	3.75/300[b]	
(+)-IXb	3860[a]	−7464/581	2.18/615	C_2H_5OH
		53480/365	3.67/340[b]	
		−8380/280	3.75/305[b]	
(+)-(*S*)-X		21400/364	3.21/339	CH_3CN
		−12600/289	3.26/297	
	375/0.045	19700/364	3.23/339	H_2O
		−13364/290	3.21/301	
		21200/363	3.29/340	0.1 *N* HCl
		−14000/289	3.30/304	

[a] Values of $[\alpha]_{436}$ for 0.05% solution in abs. EtOH. [b] Shoulder.

new positive Cotton effect near 320 nm * are observed. It should be noted that although the presence of a centre of chirality in the amino substituent in (+)-(*R*,*S*)-VIII increases the intensity of bands in the CD spectrum of this compound relative to (+)-(*S*)-VII, however, just as for (−)-(*S*)-I and (−)-(*R*,*S*)-II, these changes do not affect the general appearance of the CD curve.

The most likely reason for the change in the CD spectra of stereoisomers of aminoaldehydes I and II when protonated is a different orientation of the C=O bond of the formyl group in the predominant conformers of I and II on the one

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* This Cotton effect is probably associated with the $n-\pi^*$ transition of the formyl chromophore which, however, is not observed in the UV spectrum.

hand and VII and VIII on the other. Indeed, CD spectra of solutions of amine (+)-III in hexane and in 0.1 *N* HCl have substantially the same parameters; i.e. protonation of the amino group does not affect the sign and value of the Cotton effect of the metallocenyl chromophore (Table 3). In contrast, the formation of chelates of Cu^{II} of the type IX from optically active aminoaldehydes I and II [1,3,9] is accompanied by the same change of chirality of the metallocenyl chromophore as in protonation of these compounds. For example, (−)-(*S*)-I or (−)-(*R*,*S*)-II (negative Cotton effect at about 350 nm) and (*S*)-Ala-(*S*)-Ala form chelate of (+)-IXa or (+)-IXb, respectively, which have CD spectra showing positive Cotton effect within the same region of spectrum (Fig. 3, Table 3). On the basis of the structure of chelates of type IX determined by an X-ray study [10], the C=N group of the azomethine fragment in the chelates is oriented inwards.

As already mentioned above, in contrast to this fact, in aminoaldehydes I and II in the crystalline state the C=O bond of the formyl group is bent away from the amino substituent. It is quite probable that the orientation of the CH=O group in crystals of I and II would be retained in the predominant conformer of these compounds in solution. It follows from the above that on protonation of cymantrene aminoaldehydes, i.e. when passing from I and II to the salts VII and VIII, the carbonyl group has predominantly the *endo* orientation similar to that of the CH=N fragment in chelates IX. This conclusion is in agreement with the rule [11] which links the sign of optical rotation of chiral 1,2-substituted metallocenes with their spatial structure. Thus (*S*)-I and (*R*,*S*)-II with predominantly '*exo*' orientation of the CH=O group should and, in fact, do have a negative value of [α] [11]. On the contrary, if for the same absolute configuration of the molecule the CH=O group has a preferred *endo* orientation , the sign of [α] should be positive, which is actually

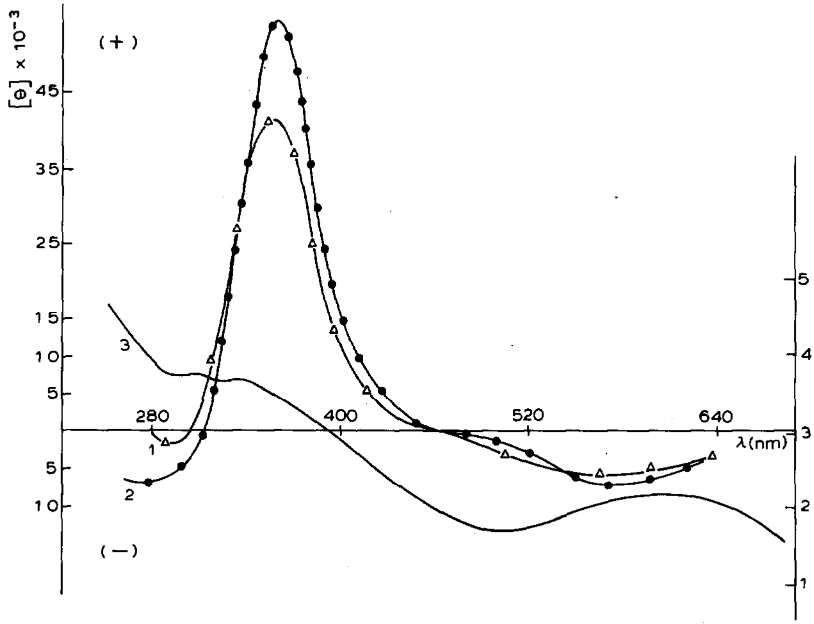
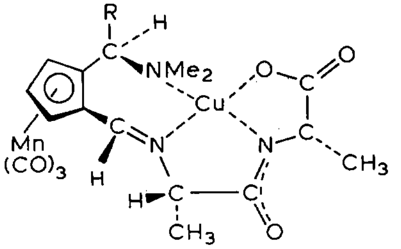
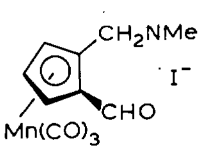


Fig. 3. CD spectra of (+)-IXa (1) and (+)-IXb (2) in C_2H_5OH and UV spectrum of (+)-IXb in C_2H_5OH.



(+)-IX: a, R = H; b, R = Me



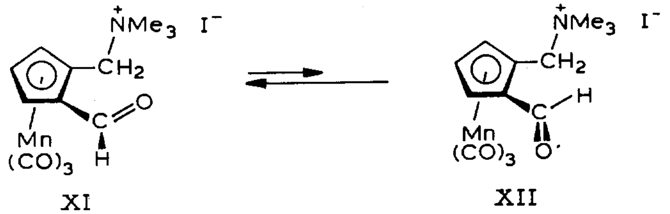
(+)-(*S*)-X

observed for both (*S*)-VII and (*R*,*S*)-VII and for (+)-IX [1,9].

One might suggest that the preferred *endo* orientation of the formyl group in protonated forms of aminoaldehydes is stabilized by formation of an intramolecular CH=O ··· H–N$^+$ hydrogen bridge in VII and VIII. In this case it would be expected that the CD spectrum of the iodomethylate of aminomethylformylcymantrene (−)-(*S*)-I (formula (+)-(*S*)-X) would be similar to the CD spectrum of (−)-(*S*)-I. However, as seen from Fig. 2 and Table 3, the number, position, signs and intensities of Cotton effects in CD spectra of (+)-(*S*)-X in CH_3CN, H_2O and 0.1 *N* HCl coincide substantially with the characteristics of the spectrum of (+)-(*S*)-VII. Therefore, a hydrogen bond of this type, is not the main reason for changing of orientation of the formyl group on protonation of I and II. In our opinion, a decisive factor influencing the change of orientation of the CH=O group is an intramolecular electrostatic interaction of the carbonyl group dipole with the positive charge of the quaternary nitrogen atom in salts of cymantrene aminoaldehydes.

Since the conformation XI of the quaternary salts VII, VIII and X should be less advantageous, for steric reasons, than the conformation XII, elevation of temperature should result in an increased contribution of the *exo* conformer XII to the conformational equilibrium of these molecules. The result of such a change should be a lowered intensity of Cotton effects in CD spectra of quaternary salts of aminoaldehydes. Indeed, on increasing temperature of a solution of (+)-(*S*)-X in CH_3CN from 22.5 to 70°C, the intensities of bands at 360 and 288 nm are lowered by 22 and 16%, respectively (taking into account the specific expansion of the solution). The observed variation of the intensities is reversible: lowering the solution temperature to the initial value results in the original spectrum being recorded.

Consequently, the data given in this paper demonstrate that the optical characteristics and the signs of Cotton effects of optically active aminoaldehydes I and II and their quaternary salts VII, VIII and X, as well as of chelates of the type of IX are determined mainly by the conformation of these molecules not depending on their absolute configuration. Therefore, it seems probable that the observed difference in intensities of the Cotton effects and [α] values for the pair



XI XII

(−)-(S)-I and (−)-(R,S)-II, as well as for the pair (+)-(S)-VII and (+)-(R,S)-VIII, is associated mainly with variation of the contributions of different conformers, distinguished by the formyl group orientation, to the conformational equilibrium as a result replacement of a hydrogen atom in the CH_2 group of the amino substituent in compounds I and VII by a larger methyl group in molecules of II and VIII. This is supported by a small but significant difference in the geometrical position of the formyl group in the molecular structures of (−)-(S)-I and (−)-(R,S)-II.

III. Orientation and stereochemistry of metallation of [α-(N,N-dimethylamino)ethyl]-cymantrene, III

The R absolute configuration of the chiral centre of the amino substituent has been previously [4] assigned to the (+)-enantiomer of III on the basis of chemical correlation and characteristics of CD and ORD spectra. As seen from Fig. 1, this assignment is entirely in agreement with the results of an X-ray analysis of (−)-(R,S)-II obtained from (+)-III by metallation. It has been already noted above that (−)-(R,S)-II is the predominant isomer of three [α-(N,N-dimethylamino)-ethyl]formylcymantrenes formed on treatment of (+)-(R)-III with n-BuLi, followed by interaction of the reaction mixture with dimethylformamide [3]. Therefore, from the data from X-ray analysis it follows that metallation of the chiral amine III, as well as of achiral (N,N-dimethylaminomethyl)cymantrene [12], is effected mainly in the 2,5-positions of the cyclopentadienyl ring. In this case, if the amino substituent has the R configuration, the attack of the metallation agent is directed mainly to the R diastereotopic C–H position of the ring. A similar stereochemistry of substitution is observed in metallation of (R)-[α-(N,N-dimethylamino)ethyl]ferrocene [13].

Experimental

Values of [α] were measured with a Polamat-A polarimeter (DDR, Yena). CD and UV spectra were obtained with a Jasco J-20 spectropolarimeter and a Specord UV-Vis spectrometer, respectively. PMR spectra were recorded with a Perkin-Elmer R-20 spectrometer (60 MHz).

Resolution of racemic I into enantiomers was carried out following a modified procedure [1] avoiding the stage of purification of the reaction products in a column with Sephadex L H-20. The synthesis of (−)-(R,S)-II was effected by the reported procedure [3] from (+)-(R)-III. Chelates (+)-IXa,b were obtained from optically pure enantiomers (−)-(S)-I and (−)-(R,S)-II, respectively, using described methods [3,9].

X-ray analysis of (−)-1-[α-(N,N-dimethylamino)ethyl]-2-formylcymantrene, (−)-(R,S)-II

Crystals of (−)-II are orthorhombic, $a = 7.461(1)$, $b = 7.652(1)$, $c = 24.696(4)$ Å, $V = 1410.0(4)$ Å^3, $M = 303.2$, $d_{calc.} = 1.44$ g/cm^3 for $Z = 4$, space group $P2_12_12_1$. The cell parameters and intensities of 2688 reflections with $I \geqslant 2\sigma$ were measured at −120°C with a Syntex P2$_1$ diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2° \leqslant 2\theta \leqslant 50°$); absorption neglected ($\mu(\lambda\text{Mo-}K_\alpha) = 9.9$ cm^{-1}). The structure was solved by the heavy-atom method and refined by the least-squares method in the full-matrix anisotropic approxmation. The final $R = 0.0361$ *. The absolute configuration was established by the Hamilton test [14]; the R factor for the inverted structure is 0.0465.

Synthesis of racemic and (+)-(S)-1-(N,N,N-trimethylammoniummethyl)-2-formylcymantrene iodides

The racemic X and optically pure (−)-(S)-X were obtained by a general procedure [4] in absolute acetone at −5°C. The yield of (±)-X is 82%, m.p. 203°C, decomp. (darkening point 200°C). Elemental analysis. Found: C, 36.16, 36.48; H, 3.51, 3.56; Mn, 12.48, 12.73; I, 29.21, 29.94. $C_{13}H_{15}NIMnO_4$ calcd.: C, 36.22; H, 3.51; Mn, 12.74; I, 29.44%.

Yield of (+)-(S)-X 81%, M.p. 217–218°C, decomp. (darkening point 207°C). Elemental analysis. Found: C, 36.00, 36.18; H, 3.80, 3.61. $C_{13}H_{15}NIMnO_4$ calcd.: C, 36.22; H, 3.51%.

Spectral characteristics of racemic and (+)-(S)-X are identical. PMR (δ, ppm, TMS extern.) in D_2O: 9.76 (s, 1H, CHO), 3.33 (s, 9H, $(CH_3)_3N^+$); in MeCN: 9.52 (s, 1H, CHO), [5.64 (m, 1H), 4.93 (tr, 1H) and 4.42 (m, 1H), protons of Cp ring]. IR in KBr 1685 (CHO), 1950 and 2030 cm^{-1} (CO).

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* Hydrogen atoms in geometrically calculated positions were included (except for hydrogen atoms of the Me group) in the refinement with fixed temperature ($B_{iso} = 4$ Å^2) and positional parameters.