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Dicobalt Hexacarbonyl Derivatives of Chiral Acetylenes†

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Abstract: $(\mu_2\text{-}RC_2R')Co_2(CO)_6$ complexes are prepared where R ≠ R' and one of these substituents is a chiral organic group. The structures of the 11 complexes (10 new) range from the simplest possible chiral acetylenic hydrocarbon derivative (S-3-methyl-1-pentyne **1a**) to ethynylsteroid (**1f**, **1g**, **1h**) and ethynylcodeine (**1i**, **1j**, **1k**) derivatives. The CD spectra are reported and the results are analysed in terms of a quadrant rule. The CD spectra show that in all complexes the $Co_2(CO)_6$ fragment of the molecule gets chirally perturbed. The reasons for the chiral perturbation include apolar repulsing (dominant for the hydrocarbon acetylenes) and polar attractive ("autosolvation"; dominant for acetylenes with polar hetero-atom containing substituents) forces.

INTRODUCTION

μ_2-Acetylenedicobalt hexacarbonyl (Co-Co) (**1**) complexes[3] have very early been identified as intermediates of C-C-coupling reactions[4]. These reactions are characterized by high degrees of chemo-[5] and regioselectivity[6]. The discovery of co-cyclizations of the coordinated alkyne in complexes **1** with CO and

† Some results of this work were presented at a Conference[1]. This work started at the Research Group for Petrochemistry, Hungarian Academy of Sciences, Veszprém (Hungary)

‡ Deceased: 1991. This paper is dedicated to his memory

olefins[4c,d,7] (Pauson-Khand reaction) and the easy generation of $(RC_2C^+)Co_2(CO)_6$ carbonium ion reagents[8] (Nicholas reaction) have placed complexes **1** among the current organic synthons.

The first derivatives **1** with chiral acetylenes (steroid derivatives) were reported[6a,8a] in the 70-ies and later these have successfully been used in biochemical studies by Jaouen et al.[9]

Recently, chiral derivatives **1** were reported[10] which could find applications in asymmetric syntheses[11].

These aspects of the chemistry of complexes **1**, prompted us to perform a systematic study on the chiroptical properties of derivatives **1** with various chiral groups in the side chain. Such complexes were earlier preferentially studied by ^{1}H-NMR techniques (e.g. ref. 10,12). Since chiroptical data had not been reported earlier we obtained CD spectra of a series of chiral derivatives **1** and undertook an attempt at correlating the chiroptical properties with reasonable conformational possibilities.

RESULTS AND DISCUSSION

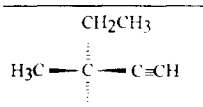
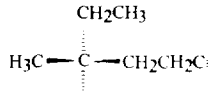
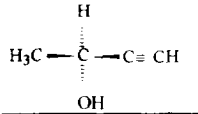
Preparation and Structure of the Complexes

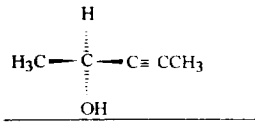
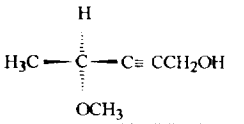
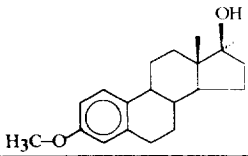
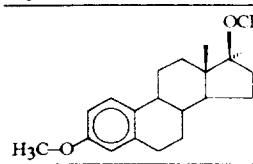
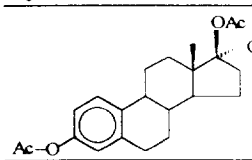
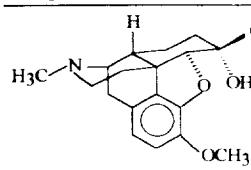
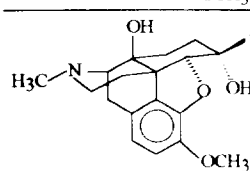
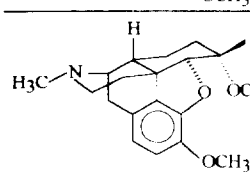
Compounds **1** were prepared by the usual[5] method: reacting the corresponding acetylene, $R^1C_2R^2$ (**2**) with octacarbonyldicobalt in n-hexane or (in the case of more polar compounds **2**) benzene solution, at room temperature, under N_2 or Ar atmosphere. The products were purified by repeated preparative TLC[13]. Yields almost appeared to be 80-95 %.

Compounds **2** of high enantiomeric purity (>95 %) were prepared as described in the Experimental Section.

Compounds **1** were characterised by analyses (c.f. Experimental), and infrared ν(C-O) absorptions (Table 1).

Table 1. Infrared ν(C-O) Spectra of Complexes $(\mu_2\text{-}RC{\equiv}CR')Co_2(CO)_6$ (**1**)

Organic ligand (2) RC≡CR'	Absorptions[a] [cm^{-1}] and assignment[b]						
	$\nu_1(A_1)$	$\nu_4(B_1)$	$\nu_6(B_2)$	$\nu_2(A_1)$	$\nu_5(B_1)$	$\nu_3(A_2)$[c]	$\nu(^{13}C\text{-}O)$
 **a**	2092.5 m	2052.5 vs	2029.7 vs	2020.2 s	2011.0 w	~2007 vw, sh	1983 vw
 **b**	2094.8 m	2056.0 vs	2030.9 s	2020.0 w, sh	2014 vw, sh	~2009 vw, sh	1977.5 vw
 **c**	2093.3 m	2057.2 vs	2033.8 s	2024.9 s	2016.1 w	~2005 vw, sh	1981 vw

 **d**	2092.0 m	2052.2 vs	2028.0 vs[d]		2018.4 s	~2008.3 w, sh	~1980 vvw
 **e**	2094.9 m	2057.0 vs	2030.5 vs	2020.0 w, sh	2016.5 w, sh	~2010.0 vw, sh	1976 vw
 **f**	2093.4 s	2054.5 vs	2034.1 vs	2022.9 s	2011.4 w, sh	~2007 vw, sh	1977.2 vw 1968 vvw, sh
 **g**	2093.4 ms	2054.8 vs	2032.0 s	2022.1 s	2010.8 mw	2005 w, sh	1979 vw
 **h**	2093.7 s	2055.3 vs	2031.9 vs	2023.2 w	~2013 sh	2011.2 w	1981 vw
 **i**	2095.7 m	2057.4 vs	2033.7 vs	2025.6 s	2015.9 w, sh	2010.4 vw, sh	1979.9 vw 1974 vvw, sh
 **j**	2095.3 m	2057.6 vs	2033.3 vs	2026.7 s	2015.1 w, sh	2011.6 vw, sh	1980.5 vw
 **k**	2096.3 m	2059.3 vs	2033 w, sh	2030.0 vs	2010.6 m	2007 vw, sh	1977.9 vw

[a] All spectra were obtained in n-hexane solution, using simultaneous DCI calibration[14]

[b] According to considerations based on refs. 15-17, using notation corresponding to C_{2v} local symmetry of the $C_2Co_2(CO)_6$ skeleton

[c] Inactive according to strict C_{2v} selection rules however, it gains intensity due to the difference in electronic effects if $R \neq R'$ [16,17]

[d] Most probably two accidentally degenerated bands in one band envelop

The ν(C-O) IR spectra of compounds **1** are characteristic in shape and band number. If $R^1 = R^2$ C_{2v} selection rules apply and thus 5 IR active modes can be observed[15] while $R^1 \neq R^2$ reduces the symmetry to C_s or C_1 that requires 6 IR fundamentals[16,17]. In the case of propargylic amines, ethers and alcohols the contour of the spectrum changes[18]; this seems to be due to the presence of various conformers corresponding to the geometry of the side chain[19a] and/or to solvation-like interaction between polar groups in the side chain and the metal carbonyl part of the molecule ("autosolvation"[10g,18,19]) or both. The assignment of the structure of compounds **1** by IR spectra is based on identical spectroscopic behaviour of **1** derivatives characterized by single-crystal X-ray diffraction measurement[20].

Optical Activity

The CD spectra of compounds **1** and **2** were obtained (Fig. 1, Tables 2, 3) together with some UV-VIS spectra. The following general features can be observed:

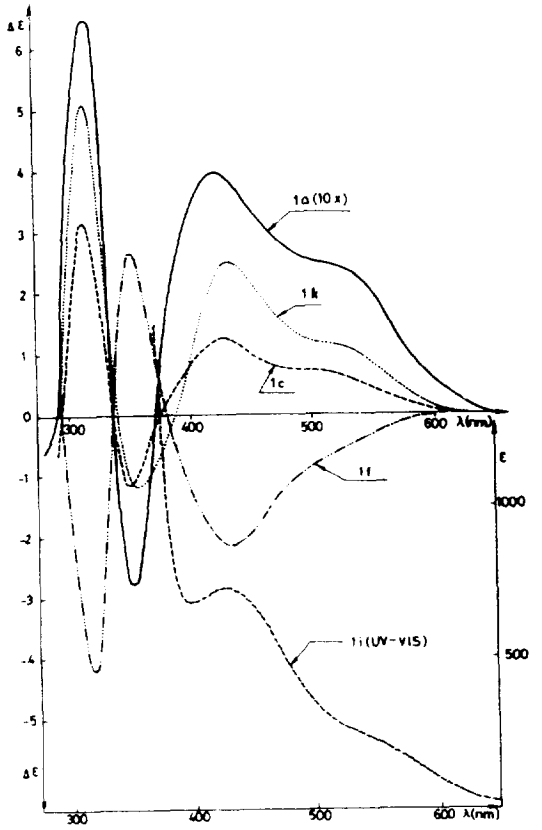


Fig. 1 Some representative CD spectra of compounds **1**. For comparison: UV-VIS spectrum of **1i**.

Table 2. CD Bands of Complexes **1** (λ > 280 nm)

Compound	Solvent[a]	λ_{max}, nm ($\Delta\varepsilon$)[b]				
1a	CH	510sh(+0.25)	427(+0.40)	352(- 0.28)	318(+0.65)	290(0)
1b	NH	510sh(+0.06)	427(+0.12)	349(- 0.07)	317(+0.29)	287(0)
1c	NH	510sh(+0.73)	428(+1.29)	350(- 1.13)	314(+3.14)	292(0)
1d	NH	544 (+0.52)	428(+0.86)	351(- 0.78)	318(+1.56)	299(0)
1e	NH	550sh(+0.07)	427(+0.33)	350(- 0.44)	314(+0.68)	292(0)
1f	CH	490sh(- 1.12)	434(- 2.14)	352(+2.67)	318(- 4.21)	295(0)
1g	CH	490sh(- 1.14)	433(- 2.16)	352(+2.86)	319(- 4.22)	296(0)
1h	CH	540sh(- 0.08)	420(- 0.57)	353(+1.06)	313(- 2.25)	
1i	CH		418(+0.86)	351(- 0.78)	318(+1.56)	290(0)
1j	CH	550sh(- 0.05)	425(- 0.35)	366(- 0.59)	317(- 2.00)	
1k	CH	510sh(+1.24)	430(+2.52)	355(- 1.17)	316(+4.91)	292(0)

[a] NH = n-hexane, CH = cyclohexane

[b] Sh = shoulder

Table 3. CD Bands of the Starting Compounds **2** (λ > 180 nm)[a]

Compound	Solvent[b]	λ_{max}, nm ($\Delta\varepsilon$)[b]			
2f	DO	284(- 0.52)	275(- 0.41)		
2g	CH	232(+2.87)			
2h	CH		205sh(- 5.83)	185(-17.07)	
2i[c]	CH	282(- 1.00)	258sh(- 0.08)	243(+2.94)	212(- 5.60)
2j[d]	CH	282(- 1.48)		244(+2.58)	217(-13.60)
2k	NH	282(- 2.9)	260sh(- 0.4)	240(+7.7)	216(-17.4)

[a] Compounds **2a-2e** did not show evaluable CD absorptions at λ > 180 nm

[b] DO = dioxane, CH = cyclohexane, NH = n-hexane, sh = shoulder

[c] Ref 21d reports: (acetonitrile) 281 (-2.53), 243(+5.04), 223(-8.96)

[d] Ref 21d reports: (acetonitrile) 282 (-2.24), 243(+2.66), 220(-5.23)

(i)Compounds **1** and **2f-2k** show CD bands in the range 290-550 nm and 210-290 nm respectively[21].

(ii)The UV spectra of compounds **1** are of similar shape as the CD spectra at λ > 300 nm.

(iii) The $\lambda > 300$ nm parts of the CD spectra of compounds **1** are similar in shape however, the intensities and the sign patterns are different for the individual compounds (Fig.1).

These aspects prompted us to confine our studies to the $\lambda > 300$ nm part of the CD spectra which can be most certainly attributed to absorptions of the C_2Co_2 and/or the $C_2Co_2(CO)_6$ moiety of the molecules[22]. Each complex showed a CD band at ~ 430 nm (approximately at the same wavelength also a broad UV/VIS band of $\varepsilon \sim 10^3$ intensity can be observed) therefore in course of the evaluation of the spectra we focused our attention mostly to the intensity and sign of this CD band.

The $C_2Co_2(CO)_6$ moiety of compounds **1** has a C_{2v} local symmetry. This is true for the whole molecule too if symmetric ligands **2** are used or reduced to C_s when $R^1 \neq R^2$, but both are symmetric to the plane determined by the acetylenic C atoms and the midpoint of the Co,Co bond. Both C_{2v} and C_s are achiral. These symmetries can further be reduced by the presence of a chiral group in the side chain by either or both of the following two mechanisms (Fig. 2).

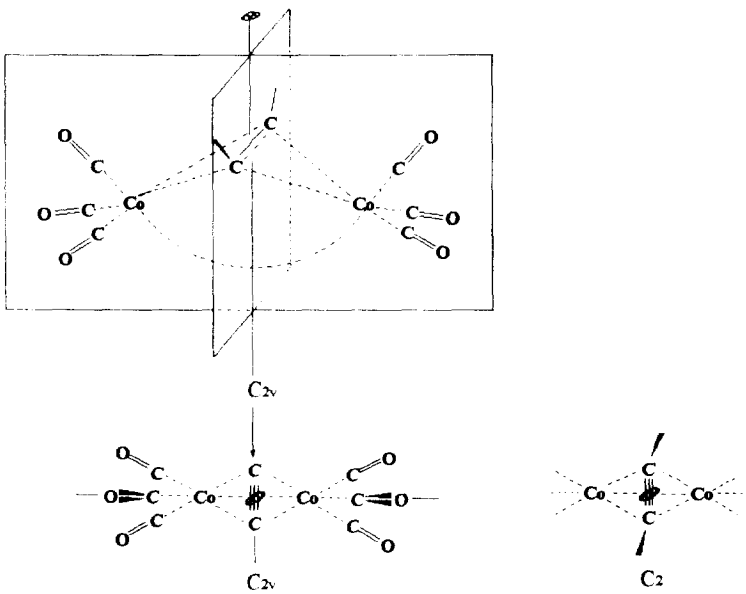


Fig. 2 Inherently achiral (C_{2v}) and inherently chiral (C_2) conformations of the chromophore.

(a) Supposing that the actual chromophore was the $C_2Co_2(CO)_6$ moiety with a C_{2v} local symmetry, the sign of the rotatory strength induced by the perturbing effect of the chiral environment can be best described by the quadrant rule[23]. The symmetry planes of the C_{2v} point group determine by all means such surfaces which cause a sign change in the contribution of a given part of molecule that penetrates through such a plane (nodal planes determined by symmetry). A more detailed sector rule would also require the knowledge of the nodal planes generated by the molecular orbitals (nodal planes determined by MO-s). Since at present

we are unable to assign the CD bands to the corresponding electronic transitions, therefore we could start our reasoning on the basis of a quadrant rule required by the C_{2v} symmetry.

(b) The coordinated "cis-planar-excited" acetylene geometry[22a,24] may be forced to a "cis-bent" array[16,17], and thus even the chromophore itself loses its specular symmetry reducing the achiral C_{2v} point group to the (inherently) chiral C_2.

Both factors can contribute to the optical activity at the same complex but the intensity of the effect of (b) is expected to be stronger than that of (a)[25].

Using chiral acetylenes (**2**) of *known* configuration and *assuming* that a *quadrant rule* (Fig. 3) was to control the optical activity of the complexes **1**, we performed our deductions on an *empirical* basis, in order to get further insight into the mechanisms responsible for the development of the low-energy CD bands ($\lambda > 300$ nm) in the spectra of complexes **1**.

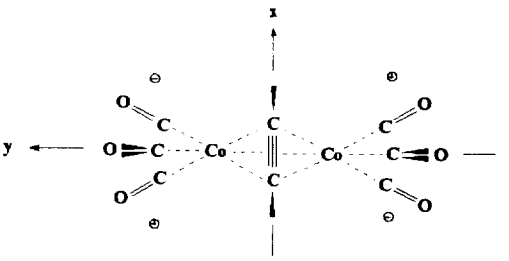


Fig. 3 Quadrant rule (at least for the upper sectors) of the $C_2Co_2(CO)_6$ chromophore.

Our first model was the simplest possible chiral acetylene hydrocarbon: 3-methyl-1-pentyne with S absolute configuration (**2a**)[26]. The possible conformers of compound **1a** are shown in Fig. 4.

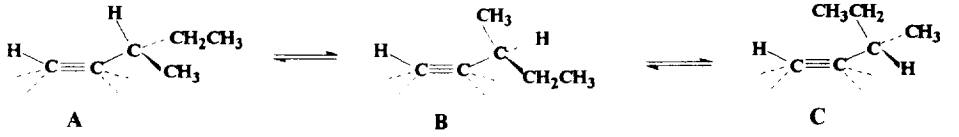


Fig. 4 Conformers of the organic ligand in **1a**.

It seems reasonable to assume that conformer **A** has the highest probability, where the more bulky alkyl groups of the chiral carbon atom are turned "outward" from the complex core. Most probably the repulsion forces between the ethyl group and the axial carbonyl group, which is near to it will push the methyl group towards the core of the complex. This situation may also cause a slight torsion of the H1-C1-C2-C3 atoms in the acetylene moiety from the planar array.

This stereochemical model was also tested by means of molecular models constructed on the basis of the reported structural data on compounds **1** and **2**[20,26,27]. A schematic view is shown in Fig. 5.

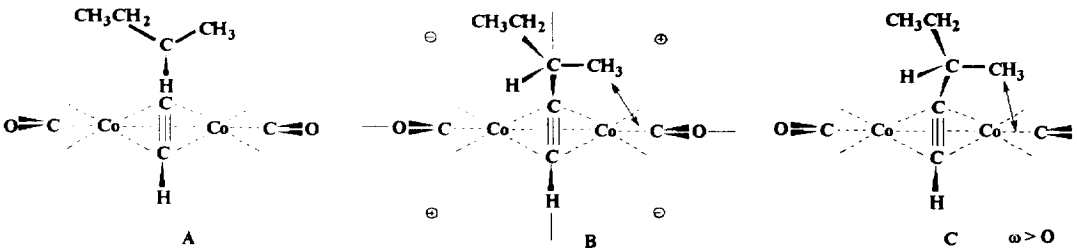


Fig. 5 Development of repulsive interactions in conformers of **1a**.

Thus, the most probable conformation involves that the methyl group gets nearer to the chromophore whereas the ethyl group will be oriented near to one of the nodal planes, and thus, it is the methyl group whose perturbing effect dominates.

In this conformation the methyl group will be situated in the "upper right" quadrant, consequently it can be supposed that the group in this quadrant represents a *positive* contribution to the sign of the first two CD bands. The signs of the rest of the quadrants can be deduced from the local C_{2v} symmetry. If the torsion of the coordinated acetylene is also taken into account a positive sign contribution to the first two bands should be assigned to a positive torsion angle (Fig. 5 structure C, $\omega>0$). This empirical rule is in good agreement with the sector rule deduced by Snatzke[21b,c,28] for the magnetically allowed electrically forbidden transitions (of $A_2 \leftarrow A_1$ symmetry) of inherently achiral chromophores which, however, have C_{2v} *local* symmetry. It can be reasonably supposed that the electronic transition which is responsible for the CD band analysed by us takes place with the participation of one of the more or less "intact" π-orbitals of the acetylene ligand (b_1) and of one cobalt *d*-orbital (b_2). This consequently satisfies the A_2 symmetry.

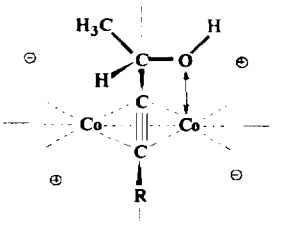
The optical activity of complex **1a** is rather weak, (the $\Delta\varepsilon$ of the ~ 420 nm band being + 0.4) considered in the spectral range. This can be explained by taking into account that the stereochemical interaction leading to the preference of conformer **A**, is relatively weak (a simple van der Waals repulsion) and therefore conformers **B** and **C** could also have a considerable population. Moreover, the perturbing effect of the apolar methyl group on the transitions of the chromophore should also be of moderate strength.

The CD spectrum of the derivative 1 of the structurally related S-5-methyl-1-heptyne (**1b**)[26] can be explained in an analogous manner, however, the greater distance of the stereogenic centre from the organometallic chromophore results in an even weaker optical activity ($\Delta\varepsilon$ ~ 420 = + 0.12).

The nature of the perturbation effect can be further studied on compounds 1 containing polar and/or very bulky groups around the centre of chirality.

Our next model - in this sense - was then the dicobalt hexacarbonyl derivative of S-3-butyne-2-ol (**1c**)[29], which is structurally similar to **1a** with the difference that the ethyl group of **1a** is substituted by an OH group in **1c**. A simple stereochemical approach would predict an optical activity for **1c** lower than for **1a**. Since the steric requirements of the CH_3 and OH groups are much nearer to each other than those of the CH_3 and C_2H_5 groups,

therefore, a decreased preference of either of the possible conformers could be expected. The experimental finding is that the shape of the CD spectrum of **1c** appears to be similar to that of **1a** but the intensity of the bands shows a 3 to 5 fold growth. This result cannot be explained only by assuming that the repulsion between the slightly larger methyl group and the nearer axial carbonyl would be the only reason of the obvious interaction of the OH group with the chromophore. It seems to be more justified to suppose that this interaction (Fig. 6) contains also an "attractive" component; a positive secondary valence interaction between the OH group and *either one* or *both* of the nearer Co atoms *and* one of the carbonyl groups coordinated to this Co atom (most probably the axial one).



1c: R = H 1d: R = CH_3

Fig. 6 Interaction between the α-hydroxyethyl group and the chromophore in **1c** and **1d**.

This interaction may be of an H-bond type[30] or a mutual donor-acceptor effect[18,19,31]. (The H-bond type interaction seems to be of limited importance on the basis of the results discussed below.) Thus, the increased optical activity is likely to be caused by the more fixed conformation of the chiral ligand, which is a result of the strong interaction between the perturbing OH group and the organometallic chromophore.

The $Co_2(CO)_6$ derivative of S-(-)-3-pentyne-2-ol (**1d**)[32] shows a CD spectrum which is similar to that of **1c**, however, it exhibits a lower intensity.

Our next model provided a good possibility to compare the influence of an OH and OMe group in the side chain. This was the type 1 derivative of S-4-methoxy-2-pentyne-1-ol (**1e**)[29b,33]. This compound shows a CD band system which is similar to the former two compounds **1c** and **1d** however, the intensity is much lower. This result can be explained in two ways.

(a) In compound **1e** the stereogenic carbon atom bears not an OH but a OCH_3 group and the latter might develop a weaker interaction with the chromophore because either of its greater steric requirements or of the lack of the possibility of hydrogen bridging.

(b) The organic ligand in **1e** has a higher constitutional symmetry than that in **1c** or **1d**: **2e** being an internal acetylene where the triple bond is situated *between two polar groups*, the chiral α-methoxyethyl and the achiral hydroxymethyl moieties. *Both oxygen* atoms could *interact* with the chromophore but *only one of these* would result in *chiral perturbation*. The transoid conformers can be expected as the more probable ones for steric reasons. The structure of the organic ligand, however, allows more than the preferred

conformers and thus, the optical activities of these can (partly) quench each other resulting in a weaker gross effect.

We believe that the second explanation fits better to the general chemical experience and the results obtained later in this study. The possible conformers of **1e** according to explanation (b) are shown in Fig. 7.

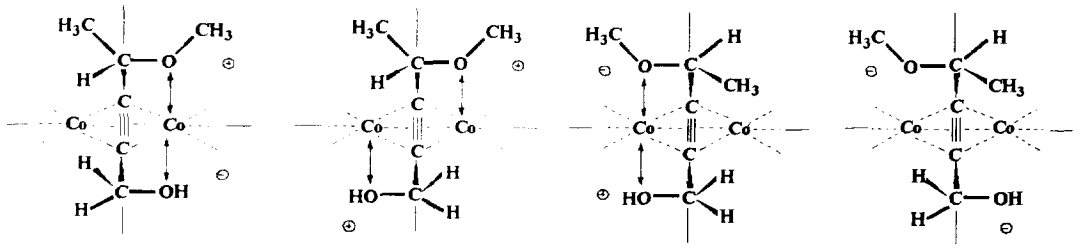


Fig. 7 Possible conformations of **1e**.

The fact that **1d** shows a higher $\Delta\varepsilon$ in the 430 nm range is also in good agreement this with explanation. Since this compound is of very similar structure with the only important difference that it does not contain an OH group in the achiral substituent of the acetylene moiety, therefore at **1d** the above encountered possibility of reduction of chirality by transoid orientation of the two oxygen-containing groups can not take place.

Our next aim has been to test the rules deduced with the relatively simple compounds **1a** to **1e** with more complicated molecules of biochemical significance.

A group of steroid derivatives containing a 17-α-(axial)-ethynyl group and 17-β-(equatorial)-OH (**1f**), -OMe (**1g**) and -OAc (**1h**) groups have represented a consistent series of models with comparable structural differences [§].

Compounds **1f**, **1g** and **1h** (in the investigated range) showed CD spectra which are similar in shape to those of the compounds discussed earlier but of higher intensity and opposite sign pattern has been noted.

Pondering about the possibilities leading to the most probable conformations, the two different environments of ethynyl group should be considered (Fig. 8), and the following statements can be made.

(a) The OR (R = H, Me, Ac) group should be placed near to one of the Co atoms (or $Co(CO)_3$ moieties).

(b) The steroid skeleton should be as far as possible from the (likewise bulky) $C_2Co_2(CO)_6$ fragment.

Both of these conditions are satisfied by conformer **A** in Fig. 8.

In conformer **A** the OR group is situated in the same quadrant as in compounds **1c-1e**. Thus the major part of the large organic ligand will thus be in a quadrant with the opposite sign. In this case it can evidently be concluded that the effect of many, however all of them weakly perturbing (more distant) atoms overcompensates the effect of the strongly perturbing OR group and the sign is determinated by the position of

[§] The structures of the A and B rings were different but according to the vast experience of CD spectroscopy of steroids[21a-c, 34] this does not influence significantly the optical activity in the D ring.

the steroid moiety. The well-known octant rule describing the $n \rightarrow \pi^*$ Cotton-effect of steroid ketones is based on a closely similar argumentation[21b,23a,35]. Since here the more extended *d*-orbitals of the metal take also part in the electronic transitions responsible for optical activity the influence of the more remote parts of the steroid ring system may be even more important in the case of the present (cobalt carbonyl) chromophore (as compared to the ketones).

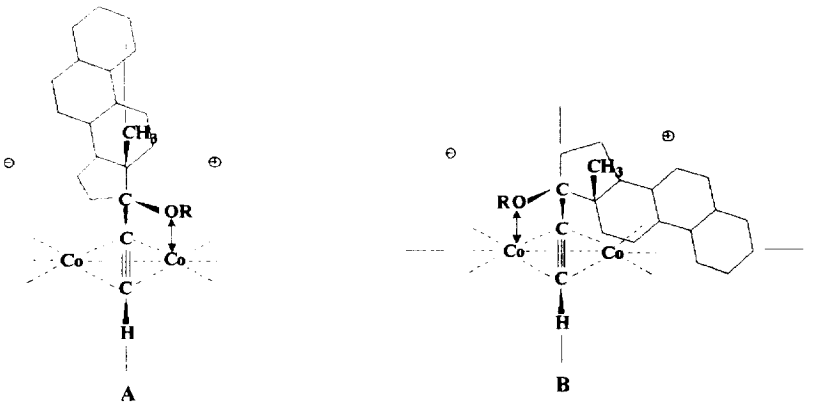


Fig. 8 Positions of the steroid moiety in the conformers of **1f** (R = H), **1g** (R = CH_3) and **1h** (R = Ac). (For rings A and B, only the carbon skeleton is indicated.)

It is an important feature of the CD spectra of the steroid derivatives that the hydroxy and methoxy derivatives **1f** and **1g** show almost identical CD patterns while the intensity of the bands of the acetoxy compound **1h** is much lower. This can be explained by supposing that the oxygen directly attached to the chiral α-carbon atom plays an important role in fixing the preferred conformer. This effect appears to be related to the Lewis basicity of that oxygen atom, that is practically equal in the OH and OCH_3 groups, but it appears much weaker in the acylated derivative. Evidently, in this interaction the oxygen is the donor and either one of the cobalt atoms or one of the coordinated carbonyl carbons[36-38] may be the acceptor partner. This behaviour indicates that H-bridging should be less important in the stabilisation of the preferred conformer(s) (c.f. also the discussion of the spectra of **1c** and **1d**).

Further instructive pieces of evidence could be obtained by means of some codein derivatives: **1i**, **1j** and **1k** [21d,39]. The configuration around the chiral centre next to the ethynyl group in starting ligands **2i**, **2j** and **2k** resembles to some extent to that of the steroid derivatives: while according to a well-founded reasoning[21d,39] the OR group of the codein derivatives is axial and the ethynyl group is equatorial (that is just the opposite as in the steroid derivatives) however, the array of the rest of the organic ligand attached to this centre of chirality (6-C) is very similar to the arrangement the steroid moiety. This is depicted schematically in Fig. 9.

Fig. 9 Schematic comparison of the configurations around the 17-C (steriod derivatives) and 6-C atoms (codein derivatives)

The codeine derivatives show CD spectra that are similar in shape and intensity to those of the steroid derivatives, at **1i** and **1j** also the sign pattern was the same, while at **1k** this was opposite.

The analysis of the spectra could best be started with that of compound **1k**, the 6-methoxy derivative. In this molecule there are two oxygen atoms in the close vicinity to the (6-C) centre of chirality: those of the 6-methoxy and of the cyclic ether group. On the basis of our earlier findings it is straightforward to suppose that both of these oxygen atoms will be situated near to one of the cobalt atoms (or $Co(CO)_3$ groups). This can be realised only in one conformation (Fig. 10) where the major part of the organic group is turned "outward", thus, it is situated in a positive quadrant. This causes the positive sign of the ~ 420 nm band and the strongly fixed nature of this conformation also results in relatively high intensity ($\Delta\varepsilon = +2.5$).

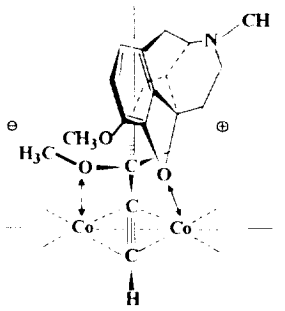


Fig. 10 Preferred conformation in **1k**

In the case of the 14-hydroxy derivative **1j** already *three* chemically very similar oxygen atoms compete for the vicinity of the *two* cobalt atoms. It can be concluded that the conformer where the OH groups are turned "inward" will be the most stable one. In this conformation (Fig. 11) a great part of the molecule (which is moreover nearer to the chromophore) will be in a *negative* sector which causes the negative sign of the ~ 420 nm band, while the less asymmetric array of the organic ligand (in the quadrants with opposite signs) causes the reduced intensity.

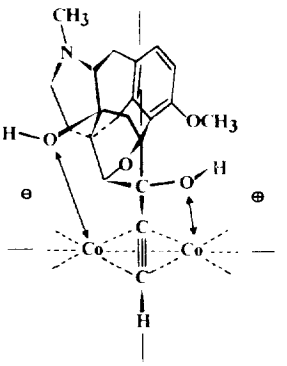


Fig. 11. Preferred conformation in **1j**

Finally, in the case of the "basic" compound, the 6-ethynyldihydro-codeine complex **1i**, a competition of the two O atoms similar to that in compound **1k** can be supposed. Obviously, the interaction of the cobalt carbonyl fragment with the sterically less hindered 6-OH group gets decisive leading to a negative sign. On the other hand, the organic ligand is less crowded than in **1k** and therefore, the preferred conformation is less fixed resulting in less intense CD bands.

CONCLUSIONS

It was found in the course of this study that (acetylene)$Co_2(CO)_6$ type complexes of chiral alkynes show chiroptical behaviour which is markedly different from that of the free ligands. The main difference is the appearance of low-energy $\lambda > 300$ nm CD bands in the complexed derivatives. These CD bands appear to be caused by chirally perturbed transitions of the $C_2Co_2(CO)_6$ fragment. The mechanism of the perturbation involves repulsive forces for acetylenes with apolar substituents or at acetylenes bearing polar groups a donor/acceptor (non-primary valence) interaction *between* the heteroatoms (O) of the substituent of the C_2 moiety *and* the metal carbonyl part of the molecule ("autosolvation"[10g,18,19]). These interactions (Fig. 12) contribute to the stabilisation of certain chiral conformers. The strength of this stabilisation seems to be between that of regular donor/acceptor bond formations and ordinary van der Waals interactions, apparently strong enough to modify the electron distribution of the $C_2Co_2(CO)_6$ fragment to induce CD activity in this achiral group. The autosolvation type stabilisation of conformers might be utilised in achieving (or promoting) asymmetric induction in syntheses involving (acetylene)$Co_2(CO)_6$ complexes.

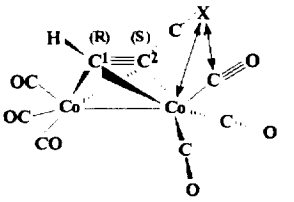


Fig. 12 Schematic representation[10g] of the mechanism of the chiral perturbation in the (μ_2-acetylene)$Co_2(CO)_6$ complexes

The appearance of the new CD bands in the spectra of complexes **1** (with respect to the free ligands **2**) provides a useful tool for the exploration of the configuration around the stereogenic centre next to the ethynyl group. This is particularly advantageous (i) if there are more CD active regions in the molecule (causing overlapping CD bands) or (ii) if the groups around the chiral centre generate bands only at very low wavelengths (as at non-conjugated hydrocarbons) which could be observed only with considerable experimental difficulties.

EXPERIMENTAL

All experiments were performed under N_2 or Ar atmosphere, using deoxygenated and dry gases and solvents[40] Chemicals were commercial products with the exception of $Co_2(CO)_8$[41] and the most of the chiral acetylenes which were known compounds, prepared, purified and controlled by published procedures (**2a** and **2b**[26]; **2c**[27a]; **2d**[27b]; **2e**[27a,c] **2g**[27d]; **2i**, **2j** and **2k**[21d,39]).

The spectra were obtained by the following instruments: IR, UR-20 and IR-75 (Carl-Zeiss Jena, Ger.) with contemporaneous DCl calibration[14]; UV-VIS, Specord UV-VIS (Carl Zeiss, Jena), CD, Jobin-Yvon Dichrograph, Mark 3.

Complexes **1** were prepared by published procedures[3,6a], generally by reacting 0.1 to 1 mmol quantities of ligand **2** with equimolar amounts of $Co_2(CO)_8$ in 10 to 50 mL of solvent. For acetylenes **2a** to **2e** n-hexane, **2f** to **2i** benzene, and **2j** and **2k** Et_2O were used as solvents. Generally reaction mixtures were homogeneous and the reaction was complete within 0.5-2 h at r.t.. Acetylenes **2i** and **2j** were not fully soluble in the reaction mixture, these were reacted somewhat longer (5-8 h) partly in suspension. The progress of the reaction was monitored by observation or measurement of CO evolution and by samples taken from time-to-time and analysed by IR spectroscopy (generally the highest wave number band of complex **1** and the bridging ν(C-O) band of $Co_2(CO)_8$ were the best probes; in the case of reaction mixtures in solvents other than n-hexane, the sample was drawn dry at r.t., the residue extracted by n-hexane and this extract was analysed).

When the IR spectra indicated, that the reaction was complete, the reaction mixture was analysed by TLC on silica plates. If this control analysis was satisfactory, purification was performed by preparative TLC (0.5 mm silica, generally eluted with the solvent of the reaction medium)[13] and the chromatographically pure fraction

was used without additional purification. Preparates **1b**, **1c**, **1e**, **1i**, **1j**, and **1k** were purified by this way. The pure products were drawn dry, redissolved in n-pentane or n-hexane and chilled to -78°C. Complexes **1f** to **1k** gave solid products (characterised by elemental analyses) others were oils, which were characterised by the analogy of their IR spectra 15-17 to those of structurally characterised (X-ray)[20] **1** derivatives.

Results of elemental analyses were as follows.

1f $C_{27}Co_2H_{26}O_8$, Found, Co 19.3, C 54.6, H 4.6; Calcd., 19.76, C 54.38, H 4.39 %.

1g $C_{28}Co_2H_{28}O_8$, Found, Co 19.2; Calcd., 19.31 %.

1h $C_{30}Co_2H_{32}O_{10}$, Found, Co 17.4, C 54.0, H 4.9; Calcd., 17.58, C 53.75, H 4.81 %.

1i $C_{26}Co_2H_{23}NO_9$, Found, Co 19.3, C 51.2, H 3.9, N 2.2; Calcd., 19.28, C 51.08, H 3.79, N 2.29 %.

1j $C_{26}Co_2H_{23}NO_{10}$, Found, Co 18.4, N 2.2; Calcd., 18.79, N 2.23 %.

1k $C_{27}Co_2H_{25}NO_9$, Found, Co 18.6, C 52.1, H 4.2, N 2.1; Calcd., 18.85, C 51.86, H 4.03, N 2.24 %.

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