Tetrahedron Vol 41, No 14, pp 2867 to 2870, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

CONDENSATION PRODUCTS OF FORMYLCAMPHOR WITH DIAMINES

STRUCTURES IN ALCOHOLIC SOLUTIONS AS DERIVED FROM UV ABSORPTION AND CIRCULAR DICHROISM SPECTROSCOPY

HANS PETER JENSEN
Chemistry Department A, Building 207, Technical University of Denmark, DK-2800 Lyngby, Denmark

(*Received in UK* 12 *March* 1984)

Abstract -The condensation products of optically active diamines with two molecules of formylcamphor have been investigated in methanolic solutions, where the formylcamphor chromophore is known to exist in the *anti* or (E) configuration. UV absorption and circular dichroism spectra are rationalised within an exciton formalism to give information about the absolute configuration.

As with chloroform solutions, where the chromophore exists in the *syn* configuration, it is demonstrated that the title compounds may achieve the low energy conformation in seemingly different ways depending on substituents. Because of the different structure of the molecule when the chromophore is in the *anti* configuration as compared with the *syn* configuration, rotational conformations with respect to the substituted ethylene bridge in the same compound may be different in CH_3OH and $CHCl_3$.

Finally "chelating solvation" in hydrogen bonding media is demonstrated through dissolution of the compounds in various alcohols.

Recently we have discussed the Schiff base condensates of various 1,2-diamines and formylcamphor with respect to structure in chloroform solutions, in which solvent we have ascertained by ^{1}H-NMR spectroscopy that the formylcamphor chromophore is in the *syn* configuration.[1-3]

It was possible to assign absolute configurations of the various condensates through comparison with spectra of Schiff bases derived from acetylacetone,[4] and to correlate temperature variations of circular dichroism spectra of various diamines with expectations derived from barriers towards rotation around the C—C bond as a function of the number and character of substituents on the carbon atoms (e.g. en < pn < 2,3-bn < stien, where en is 1,2-ethane diamine, pn is 1,2-propanediamine, 2,3-bn is 2,3-butanediamine, and stien is 1,2-diamino-1,2-diphenylethane).

In this paper we wish to discuss the molecular structures of the title compounds dissolved in methanol where they mainly exist in the tautomeric form given by Structure III of Jensen and Larsen[1] (*anti*) as deduced from ^{1}H-NMR spectroscopy.[1,5]

The fact that the formylcamphor chromophore is in an *anti* configuration complicates the way in which we may relate handedness of exciton coupled $\pi \rightarrow \pi^*$ transition dipole moments with rotational conformation of the ethylene bridge linking the chromophores together in comparison with the situation where a *syn* configuration (Structure II of Jensen and Larsen)[1] is dominant. In the latter case we may as shown earlier[4,6] take the transition moments to be almost parallel with the N—C (bridge) bonds thereby relating the position of the transition moments directly to the conformation of the ethylene bridge.

In the case of an *anti* configuration one may first of all confirm the position of the $\pi \rightarrow \pi^*$ transition dipole moment within the chromophore by an extended Hückel calculation using valence orbital ionisation energies for the diagonal elements and the Wolfsberg–Helmholtz approximation for the off-diagonal elements.[7] Such calculations predict the transition moment to be directed slightly off (*ca* 15°) the oxygen nitrogen direction and therefore, in compounds where the formylcamphor chromophore is in an *anti* configuration, the angle, between the transition moment and the N—C(bridge) bond is *ca* 110° (*cf* Fig. 1).

In the most stable isomer of *trans*-(*R,R*)-(−)$_D$-1,2-cyclohexanediamine (R-chxn) (Structure I of Larsen)[4] it is seen that the two N—C(bridge) bonds directing towards the cyclohexane ring define a right-handed screw which is consistent with the positive sign of the Cotton effect under the high energy exciton component in the absorption spectrum of the Schiff base condensate of cyclohexanediamine and acetylacetone [R-chxn(acacH)$_2$][8] (Fig. 1 of Larsen).[4] Consider now the Newman projection of R-chxn(fmcH)$_2$ with formylcamphor (fmcH) in the *anti* configuration as given in Fig. 1. This seems to be a plausible structure given that the chromophores must get close for exciton coupling as it has the methyl substituents of the camphor skeleton on the outside of the whole molecule.

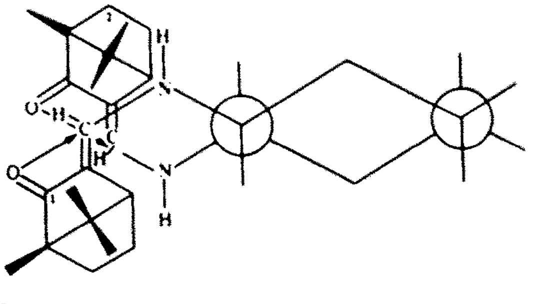

Fig. 1. Structure of R-chxn(fmcH)$_2$ with fmcH in the *anti* configuration. Ring configuration of (+)$_D$-fmcH assigned according to Allen and Rogers.[9]

With respect to handedness of the coupled $\pi \rightarrow \pi^*$ transition moments under the high energy exciton component these are seen to define a left-handed screw directing towards the cyclohexane ring contrary to the N—C(bridge) bonds which as mentioned above define a right-handed screw. Finally it is seen that the chelating solvation by one molecule of solvent to both nitrogens as proposed earlier[1] is quite plausible as the two nitrogens have their lone-pairs directed towards the empty space surrounded by the three components of the molecule.

EXPERIMENTAL

Formylcamphor, optically active diamines and condensation products of the Schiff base type were prepared as described earlier.[1,2] The identity of the condensation products was established through chemical analyses.

Absorption and circular dichroism spectra were recorded with a Cary 14 spectrophotometer and a Roussel-Jouan dichrograph II.

^{1}H-NMR spectra were recorded at 90 MHz with a Bruker HX-90 spectrometer. The ratio between *anti* and *syn* tautomers of the formylcamphor chromophore for the different condensates was established through integration of the vinyl proton signals and was in all cases found to be approximately 3 : 1, a ratio which is unchanged for several days after the dissolution in methanol of the condensates.

Abbreviations used are the same as earlier.[1-3]

Molar absorptions and circular dichroisms in the figures are given in units of $dm^3 \, mol^{-1} \, cm^{-1}$, wavenumbers are given as $10^3 \, cm^{-1}$.

RESULTS AND DISCUSSION

It is advantageous to start a discussion of dimeric exciton coupled molecules by establishing the relations between a monomeric condensate and a rigid dimeric one, and spectra of ma(fmcH) (ma = methylamin), R- and S-chxn(fmcH)$_2$ dissolved in methanol are thus shown in Fig. 2.

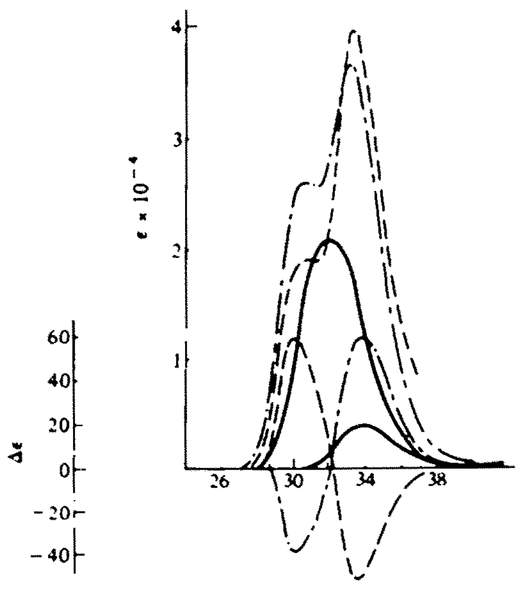

Fig. 2. Molar absorption and circular dichroism spectra of ma(fmcH) (——), R-chxn(fmcH)$_2$ (····) and S-chxn(fmcH)$_2$(–·–·–·–) in methanol.

In the case of exciton coupling between the two chromophoric parts of a dimeric molecule it was shown by Larsen[4] that the dipole strength of the dimer should be double that of the monomer. This is seen to be valid by comparing condensates of methylamine and 1,2-cyclohexanediamine either from Fig. 2 or from the data in Table 1. It is worth noting that the dipole strength of ma(fmcH) in aged $CHCl_3$ solutions is somewhat lower than in CH_3OH ($D_{chloroform} = 0.001 \times 10^{-16} \, cm^2$), but this is in agreement with Hückel calculations showing a bigger transition dipole moment within the chromophore when in the *anti* configuration than in the *syn* configuration.

Still according to Larsen an optically active dimer with strong exciton coupling should exhibit circular dichroism with rotatory strengths of opposite sign for the two transitions, and this is clearly the case for R- and S-chxn(fmcH)$_2$, which show a mirror image relationship. ma(fmcH), however, shows the inherent Cotton effect from a chromophoric $n \rightarrow \pi^*$ transition, as this circular dichroism band, besides being considerably displaced from the absorption band maximum, is found at the same place and with almost the same magnitude independently of the chromophore being in the *anti* configuration or in the *syn* configuration.

From the negative sign of the Cotton effect under the high energy component in the absorption of R-chxn(fmcH)$_2$ when dissolved in CH_3OH, it may be concluded that the configuration of the compound is as given in Fig. 1, and from the mirror image relationship between R- and S-chxn(fmcH)$_2$ it is furthermore concluded that the cyclohexane ring determines the stereochemistry of this type of compound. The finer details of the exciton coupling in the two diastereoisomers are not exactly the same as seen from the spectra of Fig. 2. Differences are, however, to be expected since the methyl groups on the camphor skeleton in S-chxn(fmcH)$_2$ must be directed towards each other when the transition moments of the high energy exciton couplet in this compound have to define a right-handed screw.

Table 1. Experimental dipole strengths of Schiff base condensates between amines and formylcamphor dissolved in methanol

Amine	Dipole strength of $\pi \rightarrow \pi^*$ transition band[4] ($10^{-16} \, cm^2$)
ma	0.0013
R-chxn	0.0027
S-chxn	0.0028
R-pn	0.0027
S-pn	0.0026
R-2,3-bn	0.0027
S-2,3-bn	0.0026
R-stien	0.0030
S-stien	0.0032
en	0.0027
ibn	0.0025
R,S-chxn	0.0027
R,S-2,3-bn	0.0027
R,S-stien	0.0030
tn	0.0028

With the rigid dimeric basis at hand we will now discuss R- and S-pn(fmcH)$_2$ and R- and S-2,3-bn(fmcH)$_2$, and as these R- and S-compounds behave similarly everything said about R-pn(fmcH)$_2$ will also be true for R-2,3-bn(fmcH)$_2$ etc. Spectra are given in Fig. 3 and dipole strengths in Table 1.

Both of the two sets of compounds show exciton splitting in the absorption spectra, and judging by the negative sign of the high energy circular dichroism band, R-pn(fmcH)$_2$ and R-2,3-bn(fmcH)$_2$ show the same rotational conformation of the substituted ethylene bridge as does R-chxn(fmcH)$_2$ (*cf* Fig. 1).

It is to be expected that the chromophores in S-pn(fmcH)$_2$ may turn to be in such a position that the camphor methyl groups do not collide. The result is, as may be seen from Fig. 3, that an equilibrium between the possible rotamers is established as identified by rather uncharacteristic circular dichroism spectra.

We may now proceed a step further and make the barrier towards rotation around the ethylene bridge high by looking at R- and S-stien(fmcH)$_2$, the spectra of which are given in Fig. 4. As with the cyclohexanediamine derivatives we see an approximate mirror image relationship between R- and S-stien(fmcH)$_2$.

To complete the picture we also consider spectra of condensates of *meso* and optically inactive diamines with formylcamphor. The spectra in Fig. 5 are those of en(fmcH)$_2$, ibn(fmcH)$_2$, R,S-chxn(fmcH)$_2$ and R,S-2,3-bn(fmcH)$_2$. The absorption spectra show clearly that exciton couplings are present in the compounds, but certainly also that the couplings in the different cases are achieved in non-equivalent ways. All of the circular dichroism spectra show a positive peak under the low energy component in the absorption spectra but they are somewhat uncharacteristic with respect to exciton coupling.

We may finally consider the spectra of R,S-stien(fmcH)$_2$ and tn(fmcH)$_2$ (tn = 1,3-propanediamine). These compounds show absorptions with no exciton splitting and circular dichroism spectra twice that of ma(fmcH). This reflects, for tn(fmcH)$_2$ that the two chromophores have a large spatial separation and consequently do not couple, and for R,S-stien(fmcH)$_2$ that the compound exists as a *trans* rotamer with respect to the substituted ethylene bridge whereby the chromophores achieve large spatial separation with no exciton coupling as a result.

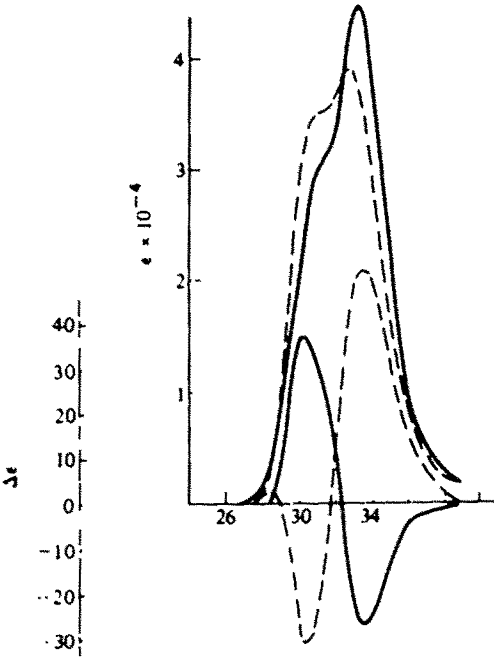

Fig. 4. Molar absorption and circular dichroism spectra of R-stien(fmcH)$_2$ (—) and S-stien(fmcH)$_2$ (-) in methanol.

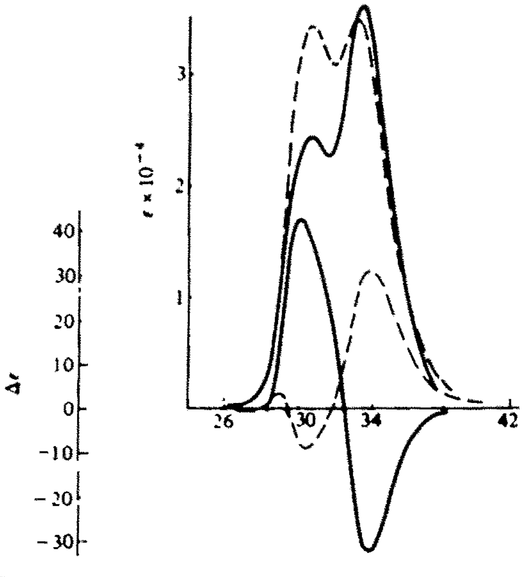

Fig. 3. Molar absorption and circular dichroism spectra of R-pn(fmcH)$_2$ and R-2,3-bn(fmcH)$_2$ (—) and of S-pn(fmcH)$_2$ and S-2,3-bn(fmcH)$_2$ (- -) in methanol.

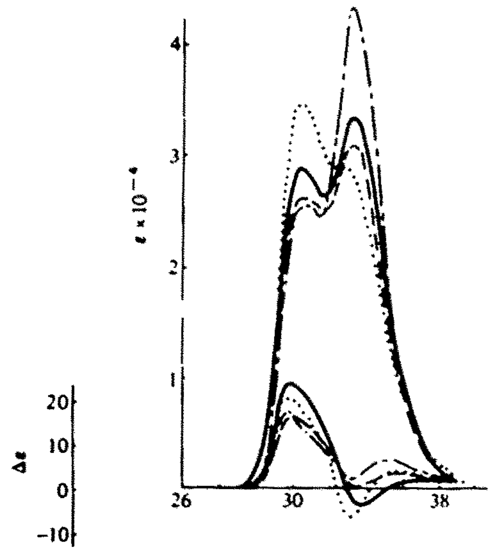

Fig. 5. Molar absorption and circular dichroism spectra of en(fmcH)$_2$ (——), ibn(fmcH)$_2$ (-- -), R,S-chxn(fmcH)$_2$ (-·-·-·-) and R,S-2,3-bn(fmcH)$_2$ (....) in methanol.

As mentioned above we have tentatively suggested that the solvation for Schiff bases of 1,2-diamines and formylcamphor is of a special nature, e.g. such that one solvent molecule may coordinate to both nitrogen atoms of the condensates when in a *gauche* conformation. This suggestion emerges on the basis of the rather large energy separation of the two exciton transitions and needs further verification.

In Fig. 6 are shown spectra of R- and S-pn(fmcH)$_2$ when dissolved in 2-methyl-propan-2-ol (*tert*-butyl alcohol) and these spectra should, in connection with a discussion of chelating solvation, be compared with the spectra of Fig. 3. It is obvious from this set of spectra that the distribution between various rotamers is quite different for a given compound in the two alcohols.

It may from the absorption spectra and using eqn (3) of Ref. 4 be concluded that the angle between the two $\pi \rightarrow \pi^*$ transition moments in the dimeric Schiff base molecules is different in the two alcohols, the angle being smallest in methanolic solution, as it is also expected to be in the case of chelating solvation in methanol, solvation which is not possible in *tert*-butyl alcohol due to steric hindrance.

Chelating solvation should force the two chromophores towards each other and consequently we expect a greater splitting in methanol than in *tert*-butyl alcohol, which expectation is confirmed by experiment [R-pn(fmcH)$_2$: $\Delta E_{\text{methanol}} = 2670$ cm^{-1}, $\Delta E_{\text{butanol}} = 2430$ cm^{-1}; S-pn(fmcH)$_2$: $\Delta E_{\text{methanol}} = 2770$ cm^{-1}, $\Delta E_{\text{butanol}} = 2610$ cm^{-1}].

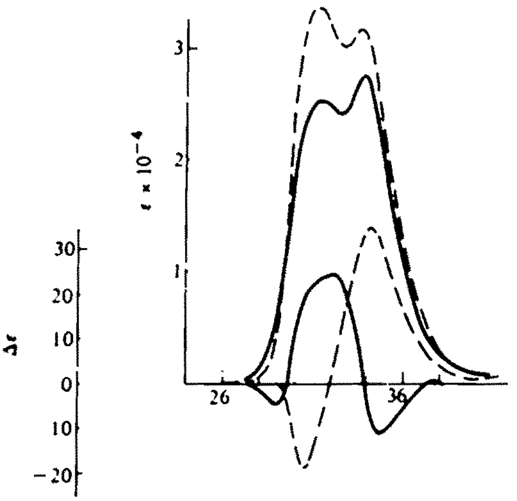

Fig. 6. Molar absorption and circular dichroism spectra of R-pn(fmcH)$_2$ (——) and S-pn(fmcH)$_2$ (- - -) in *tert*-butanol.

The circular dichroism spectra, S-pn(fmcH)$_2$ behaves more characteristically of exciton coupling in *tert*-butyl alcohol than in methanol whereas R-pn(fmcH)$_2$ behaves less so, and this behaviour is general for the compounds of (*S*) and (*R*) absolute configurations, respectively.

Obviously the ideal situation for dimeric Schiff base condensates of (+)$_D$-formylcamphor and diamines (maximum exciton coupling) occurs with diamines of *R* absolute configuration in combination with chelating solvation. Whenever the chelating solvation is impossible several rotamers exist in solution as judged from the uncharacteristic shape of the circular dichroism spectra.

With respect to condensates of diamines with *S* absolute configuration these seem to have the best defined low energy structure when there is no chelating solvation to force the chromophoric groups and thereby methyl groups on the camphor skeletons towards each other.

CONCLUSION

It has been demonstrated that different derivatives of formylcamphor and diamines when dissolved in methanol (with the formylcamphor group in the *anti* configuration) have structures which may be explained using an exciton formalism provided that the asymmetric bulk of the camphor skeleton is taken into consideration.

Acknowledgement—Mrs. Lise Penzien is thanked for valuable assistance.

REFERENCES

[1] H. P. Jensen and E. Larsen, *Acta Chem. Scand.* **A29**, 157 (1975).
[2] H. P. Jensen and E. Larsen, *Gazz. Chim. Ital.* **107**, 143 (1977).
[3] H. P. Jensen, *J. Indian Chem. Soc.* **59**, 1387 (1982).
[4] E. Larsen, *Acta Chem. Scand.* **23**, 2158 (1969).
[5] E. W. Garbish, *J. Am. Chem. Soc.* **85**, 1696 (1963).
[6] N. Bernth, E. Larsen and S. Larsen, *Tetrahedron* **37**, 2477 (1981).
[7] C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*. Benjamin, New York (1964).
[8] J. A. Schellman, *Acc. Chem. Res.* **1**, 144 (1968).
[9] F. H. Allen and D. Rogers, *J. Chem. Soc. B* 632 (1971).