

Acetylcamphor Condensed with Amines. The Structure in Solution as Obtained by NMR, UV Absorption and Circular Dichroism Spectroscopy

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The structures of Schiff base type condensation products of various 1,2-diamines with acetylcamphor are rationalized within the molecular exciton theory to give information about the relative orientation of the two camphor groups. It is shown that condensation products of acetylcamphor resemble acetylacetone analogues, and consequently indirect information is obtained about the cause of the stereochemical complexity of Schiff base condensates of formylcamphor.

Recently Schiff base type condensation products of various β -diketones and diamines have been investigated and the molecular structure in solution rationalized, *e.g.* within the molecular exciton theory.^{1–4} It was, however, shown that erroneous conclusions were drawn relying on the exciton theory alone and omitting an independent check on the chromophore configuration itself. Consequently assignments of molecular structure based on Schiff bases (really enamines) of acetylacetone, which have $\pi \rightarrow \pi^*$ transitions polarized approximately in the N–O direction in a planar *syn* or (*Z*) structured chromophore with intramolecular hydrogen bonding, will be erroneous if the tautomer distribution for some β -diketones is different from that of acetylacetone. This was exactly the case when comparing Schiff bases of formylcamphor and acetylacetone in hydrogen bonding media (*e.g.* methanol), since for the former it was demonstrated through NMR-measurements that the chromophore took on an *anti* or (*E*) structure of the ketoenamine, which in non-hydrogen bonding media, however, could rearrange to the *syn* tautomer.

The basis in the study of rotational conformations around a substituted ethylene-bridge in condensates of planar *syn* structural β -diketones and 1,2-diamines is the strong exciton coupling taking place in the molecules where the chromophores are *gauche*. This leads to a splitting of the UV absorption band, and from the circular dichroism connected to the exciton transitions of optically active dimers it is determined which chiral rotamer is dominating in solution. Details about the method and reservations about its quantitative application have been given earlier.^{1–3}

Even with the structural problem of the formylcamphor chromophore solved it is difficult to elucidate the general trends of the overall structure of the Schiff bases in terms of interactions between the asymmetric bulky β -diketone and substituents on the ethylene-bridge linking two chromophores together. To clarify whether the complexity of the formylcamphor Schiff bases compared with the acetylacetone condensation products has its origin in the asymmetric bulkiness of the camphor skeleton or in the lack of a methyl group on the side chain carbonyl group, the Schiff base condensates of acetylcamphor have been investigated.

EXPERIMENTAL

Preparations of optical active amines, acetylcamphor and Schiff base condensation products were all according to the known simple procedures.^{1,2,5} The identity of the compounds was established from chemical analyses and NMR-spectra. Circular dichroism spectra were obtained with a Roussel-Jouan Dichrographe II and absorp-

tion spectra with a Cary 14 spectrophotometer. ^{13}C NMR spectra were recorded at 22.63 MHz with a Bruker WH 90 and ^1H NMR spectra at 90 MHz with a Bruker HX-90 E.

Abbreviations

Diketones. acacH = acetylacetone (2,4-pentanedione); acH = 3-acetylcamphor, fmcH = 3-formylcamphor, both from (+)_D-camphor.

Amines. ma = methylamine; en = 1,2-ethanediamine; R-pn = (R)-(–)_D-1,2-propanediamine; S-pn = (S)-(+) _D-1,2-propanediamine; R-chxn = *trans*-(R,R)-(–)_D-1,2-cyclohexanediamine.

Condensates. R-pn(acCH)₂ etc. symbolizes the Schiff base condensate formed from one molecule of diamine and two molecules of diketone.

RESULTS AND DISCUSSION

First of all it is appropriate to investigate whether the Schiff base condensation between acetylcamphor and amines is analogous to the condensation between formylcamphor and amines, *i.e.*, occurring at the acetyl group. For this purpose ^{13}C NMR spectra were recorded using CDCl_3 as medium. The chemical shift relative to TMS of the carbonyl carbon atom in camphor is 218.4 ppm;⁶ acetylcamphor, however, shows four peaks in the carbonyl carbon resonance region, namely 211.9(193), 210.7(132), 203.8(121) and 200.1(222) all ppm relative to TMS and with relative intensities given in parentheses. This reflects keto and enol tautomers in solution and the data may be correlated with investigations on acetylcamphor in CCl_4 using the ^1H NMR technique⁷ resulting in a percentage distribution of tautomers as follows: 67% keto form and 33% enol form with intramolecular hydrogen bonding (*syn* form). From these data combined with peak intensities in the ^{13}C NMR spectrum and with knowledge of chemical shifts for carbonyl carbon atoms in acetone and acetylacetone⁶ (acetone: 206.0 ppm; acetylacetone, keto: 201.9 ppm, enol: 191.4 ppm) the following assignments are made to the peaks in the ^{13}C NMR spectrum of acetylcamphor:

- 211.9 ppm: camphor carbonyl carbon atom in keto form
- 210.7 ppm: camphor carbonyl carbon atom in enol form
- 203.8 ppm: acetyl carbonyl carbon atom in enol form
- 200.1 ppm: acetyl carbonyl carbon atom in keto form

By condensing ethylenediamine with two molecules of acetylcamphor [$\text{en}(\text{acCH})_2$] and measuring the ^{13}C NMR spectrum, which shows 13 peaks, it is demonstrated that only one tautomer is present in solution (CDCl_3). The carbonyl signals of acetylcamphor are now observed at 205.3 and 152.9 ppm (relative to TMS), the latter assignable to an enamine group and the former to a carbonyl group. Returning to acetylacetone and its Schiff bases [*e.g.* $\text{en}(\text{acacH})_2$] a shift in the carbonyl position from 201.9 to 194.9 ppm is observed by condensation; furthermore the camphor carbonyl carbon atom is found at 205.8 ppm in condensation products between amines and formylcamphor. Consequently the signal at 205.3 ppm in the ^{13}C NMR spectrum of $\text{en}(\text{acCH})_2$ is assigned to the camphor carbonyl carbon atom from which it follows that the condensation between acetylcamphor and amines occurs at the acetyl group.

To clarify whether a *syn/anti* tautomerisation depending on solvent is operative for acetylcamphor as was found in the case of formylcamphor,^{2,3} ^1H NMR spectra were measured and no variation with time and/or solvent was found. The chemical shift of the amine protons in, *e.g.*, $\text{en}(\text{acCH})_2$ is 9.0 ppm relative to TMS, *i.e.* typical of hydrogen bonding; the peak furthermore carries the full intensity of two protons thus reflecting a *syn* structure of the chromophore as the only species present in solution. Consequently with Schiff bases of acetylcamphor it is possible to make structural assignments in the strong exciton coupling limit directly from electronic spectra.

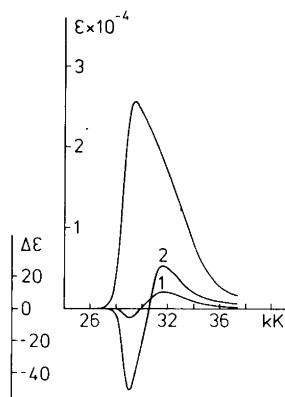


Fig. 1. Molar absorption and circular dichroism of $\text{en}(\text{acCH})_2$ in CHCl_3 (1) at room temperature and (2) at -60°C .

Table 1. Wavelength of absorption maxima and the associated molar absorptivity to the left and corresponding circular dichroism data to the right.

Compound	Abs λ nm	$D \times 10^{19}$ $\text{cm}^3 \text{cm}^{-1}$	CD			
			λ nm	$\Delta\epsilon$	λ nm	$\Delta\epsilon$
ma(accH)	314	0.9	326	4.3		
en(accH) ₂	340	1.8	344	-5.9	316	10.9
R-pn(accH) ₂	340	1.9	342	-84.4	311	35.3
S-pn(accH)	340	1.9	342	80.2	301	-33.3
R-chxn(accH) ₂	340	2.0	344	-71.5	314	28.5

Spectra of representative condensation products are given in Figs. 1 and 2 and in Table 1.

Compared with previous results on acetylacetone¹ the present spectra certainly demonstrate that both in acetylacetone and in acetylcamphor condensation products of 1,2-diamines it is the asymmetry of the diamine which is the stereochemically determining factor since the same rotamers exist for the same stereoisomeric diamine condensed with the two different diketones.

The structural assignments to acetylcamphor condensates are seen to be quite straightforward as the set of formulae derived by Larsen¹ for the strong exciton coupling limit is obeyed, *i.e.* the dipole strength of a dimer is double the dipole strength of a monomer and an optically active dimer exhibits circular dichroism with rotatory strengths of opposite signs for the two transitions.

As acetylcamphor is, however, asymmetric in itself there is also stereochemical induction from

that group. This is seen in the CD spectrum of en(accH)₂ at low temperature (Fig. 1), since the character changes from a spectrum typical of intrinsic $n \rightarrow \pi^*$ transition to a spectrum typical of exciton splitting originating from compounds with (*R*) asymmetric carbon atoms (*i.e.* Δ). This behaviour is different from what was found with en(fmCH)₂ in which the low energy rotamer seems to be of Λ configuration even though *R*- and *S*-pn(fmCH)₂ have the same and opposite low energy configuration (Δ).

The difference in behaviour between en(fmCH)₂ and en(accH)₂ must be attributable to the additional methyl group on the carbonyl chromophore in the latter compound in which the methyl group influences the way en(accH)₂ achieves minimum potential energy. The interaction between the camphor groups is greater for condensation products of formylcamphor compared with condensation products of acetylcamphor as the methyl groups in the latter case prevent close contact.

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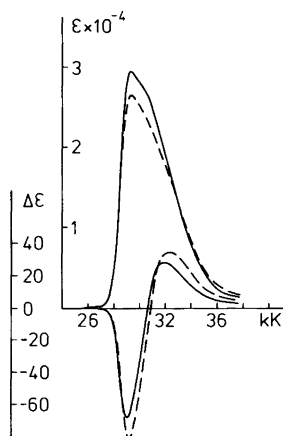


Fig. 2. Molar absorption and circular dichroism of R-chxn(accH)₂ (—) and R-pn(accH)₂ (---) in CHCl₃.