Stereochemistry in Solution of Some Schiff Bases of 1,2-Diamines with two Molecules of β-Diketones as Obtained from UV Absorption and Circular Dichroism Spectra

ERIK LARSEN

Chemistry Department I, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

From the UV absorption and the use of exciton theory it is concluded that Schiff bases of 1,2-diamines with two molecules of β-diketones in solution take on a *synagogue* rotational conformation of the bridge. For some asymmetric Schiff bases the absolute configuration of the most stable isomer has been determined from circular dichroism spectra. The *syn* conformation is shown to be a consequence of a dipole-dipole attraction. Asymmetry in the parent diamine or diketone determines which of the possible *syn* rotamers are formed.

The origin of the electronic transition in acetylacetone is so well understood that it seems reasonable to base an investigation of molecular geometry of molecules similar to acetylacetone on the study of the corresponding ultraviolet absorption.[1] The motivation for such a study comes from an attempt to assign all transitions in, for example, the copper(II) complexes of acetylacetone and of the Schiff bases of two molecules of acetylacetone and one molecule of ethylenediamine. For such complexes it should be possible to isolate or construct the spectrum arising from the ligand part in the correct steric arrangement of the complex but without the metal. The problem becomes simply the case of a dimer if the two isolated parts of the ligand system are as well understood as stated. Here, the molecular exciton theory [2] will be used to rationalize the observations on the "dimeric" Schiff bases. In a later communication also results obtained for copper(II) and nickel(II) complexes will be rationalized within this framework. A preliminary account of the results has been published.[3]

EXPERIMENTAL

References to the preparations and the analytical results are given in Table 1. Abbreviations used throughout are also explained in this table. S-polam(acacH) has been prepared by mixing molar ratios of (S)-1-amino-2-propanol and acetylacetone and heating (60—80°C) for 2 h. The product was recrystallized from benzene and hexane. All starting materials were of analytical grade.

Ultraviolet spectra were measured with a Cary 14 spectrophotometer and the circular dichroism was recorded with a Roussel-Jouan dichrograph. All measurements refer to methanol solutions.

Table 1.

Amine	Diketone	Abbreviation	Calc. composition			Found		
			C	H	N	C	H	N
(R)-1,2-Propanediamine [6]	acetylacetone	R-pn(acacH)$_2$[5]	65.5	9.23	11.75	64.92	8.98	11.68
1,3-Propanediamine	»	tn(acacH)$_2$[6]	65.5	9.23	11.75	64.50	8.98	11.88
(R)-*trans*-1,2-Cyclohexanediamine	»	R-chxn(acacH)$_2$[7]	68.8	9.35	10.06	68.57	9.14	9.89
(S)-1-Amino-2-propanol [8]	»	S-polam(acacH)	61.2	9.56	8.92	60.47	9.22	8.89
1,2-Ethanediamine	formylcamphor[a]	en(fmcH)$_2$[9]	75.0	9.38	7.29	75.20	9.44	7.04
(R)-1,2-Propanediamine	»	R-pn(fmcH)$_2$[9]	75.4	9.55	7.04	75.05	9.60	6.99

[a] Formylcamphor prepared from natural $(+)_D$-camphor.

RESULTS AND DISCUSSION

The $\pi \rightarrow \pi^*$ transition in the monomers. The acetylacetone molecule in the conjugated tautomeric form shows an intense absorption band with maximum at 34.2 kK due to the first allowed $\pi \rightarrow \pi^*$ transition. It has been shown that this transition is polarized in the oxygen-oxygen direction as predicted from calculations.[10]

The Schiff base of 1-amino-2-propanol and acetylacetone (polam(acacH)) serves as a crystalline, monomeric model-molecule for the dimeric Schiff bases under discussion. This compound exhibits an absorption maximum at 32.1 kK with a transition dipole strength of 1.2×10^{-19} cm^{-1} cm^3. Hückel MO calculations with standard parameters[11] have been performed. These calculations predict the transition dipole moment directed only slightly off the oxygen-nitrogen direction.

Predictions for the $\pi \rightarrow \pi^*$ transitions in the dimers.[2,12] In a chromophoric dimer, for example the Schiff base of $(-)_D$-*trans*-1,2-cyclohexanediamine and acetylacetone, R-chxn(acacH)$_2$, the absorption near 32 kK is split due to electrostatic coupling of the electronic transitions. The exciton theory has in many cases offered good explanations of the interactions in such weakly (not overlapping) interacting chromophores and will be used here.

Calling the ground and excited state of the monomer ψ_0 and ψ_N and denoting the two parts of the dimer A and B, the ground (Ψ_0) and excited wave-functions for the dimer will be

$$\Psi_0 = \psi_0{}^A \psi_0{}^B, \quad \Psi_a = \psi_N{}^A \psi_0{}^B, \quad \Psi_b = \psi_0{}^A \psi_N{}^B$$

In the absence of electron transfer between the two chromophores in the dimer Ψ_a and Ψ_b interact only through a coupling of nuclear vibration and electronic motion. These couplings result in two excited states Ψ_+ and Ψ_-. The signs refer to the form of the total wave-function being a vibrational wave-function multiplied by Ψ_a plus or minus Ψ_b. For the molecules we shall deal with here the vibrational structure is smeared out at room temperature and for convenience we set

$$\Psi_{\pm} = (\Psi_a \pm \Psi_b)/\sqrt{2}$$

thus omitting the vibrational parts. This treatment is suitable for the so-called strong coupling where the splitting of the electronically excited states mentioned below is large compared to the bandwidths.

The intensity of the transition $\psi_0 \rightarrow \psi_N$ is measured in the terms of the transition dipole strength

$$D = \frac{3\,h\,c\,2.3 \times 10^3}{8\,N\,\pi^3} \int \frac{\varepsilon}{\nu}\,d\nu = 91.8 \times 10^{-40} \int \frac{\varepsilon}{\nu}\,d\nu\ \text{erg cm}^3$$

or with the energy expressed in cm^{-1}:

$$D = 46.2 \times 10^{-24} \int \frac{\varepsilon}{\nu}\,d\nu\ \text{cm}^{-1}\text{cm}^3 \tag{1}$$

D is theoretically given by the square of the transition dipole moment:

$$D = P^2 = |\langle \psi_N | er | \psi_0 \rangle|^2$$

In the dimer the transition dipole moments will be

$$P_{\pm} = (P_A \pm P_B)/\sqrt{2}$$

and thus the dipole strengths of the two resultant transitions are

$$D_{\pm} = (|P_A|^2 + |P_B|^2 \pm 2|P_A||P_B|\cos\theta)/2$$

where θ is the angle between the transition dipoles of the two monomer parts. It follows that the total dipole strength

$$D_{\text{dimer}} = D_+ + D_- = 2D_{\text{monomer}} \tag{2}$$

and

$$\tan^2\theta/2 = D_-/D_+ \tag{3}$$

An optically active dimer exhibits circular dichroism with rotatory strengths of opposite signs for the two transitions:

$$R_{\pm} = \mp \frac{\pi\nu}{c}(P_A \times P_B)R_B \tag{4}$$

where R_B is the vector from the dimer center of gravity to the monomer B center of gravity of the transition moments.[13] Experimentally the rotatory strengths are expressed similarly to the dipole strengths

$$R = \frac{91.8 \times 10^{-40}}{4} \int \frac{\Delta\varepsilon}{\nu}\,d\nu\ \text{esu cm erg/gauss}$$

or with the energies expressed in cm^{-1} and ν substituted with the transition energy

$$R_{\pm} = -\pi \, E_{\pm} \, (P_A \times P_B) \, R_B = \frac{46.2 \times 10^{-24}}{4} \, \frac{\Delta\varepsilon}{\nu} \, d\nu \, cm^{-1}cm^3 \qquad (5)$$

The energy separation of the excited states for a purely coulombic interaction is given at small distances as the interaction energy between the two transition dipole moments:

$$\Delta E = E_+ - E_- = 2 \left[\frac{P_A P_B}{|r_{AB}|^3} - 3 \, \frac{(P_A \cdot r_{AB})(P_B \cdot r_{AB})}{|r_{AB}|^5} \right]$$

For the molecules considered here $|P_A| = |P_B|$, thus giving

$$\Delta E = 2 \, \frac{D_{monomer}}{r_{AB}{}^3} \, (\cos\theta - 3 \, \cos\varphi_A \, \cos\varphi_B) \qquad (6)$$

where φ_A and φ_B are the angles between the transition moments and the vector r_{AB} directed from chromophoric center of gravity of A to that of B.

Discussion of the results for the dimeric Schiff bases. The above given formulae connect the magnitude of the observables with the molecular geometry. However, the number of observables is less than the geometric parameters and further neither ΔE nor D_-/D_+ can be determined accurately from room temperature absorption measurements. Therefore, it will be demonstrated that the results for R-chxn(acacH)$_2$ are in agreement with the expected conformation and then we make correlations with very similar structures and spectra.
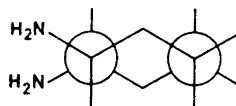
I

The most stable isomer of (R)-*trans*-1,2-cyclohexanediamine has the structure I and it is assumed that in the Schiff base the ring conformation is unchanged. In Fig. 1 the absorption and circular dichroism spectra of R-chxn(acacH)$_2$ are shown together with the absorption of the monomer S-polam(acacH). The latter molecule exhibits no circular dichroism in the spectral range (corresponding to the $\pi \rightarrow \pi^*$ transition) as expected for a planar chromophore. The experimental energy splitting of the dimer transitions is estimated to *ca.* 2 kK which is the right order of magnitude for a *syn* conformation. The total dipole strength of the bands is 2.22×10^{-19} $cm^{-1}cm^3$, which, within experimental uncertainty, is twice that of the monomer polam(acacH). Thus eqn. 2 is fulfilled.

The transition moments are expected to be nearly parallel to the nitrogen-carbon(bridge) bonds and therefore they form a pair of vectors which define a right handed screw. The in-phase transition ($\Psi_0 \rightarrow \Psi_+$) should then have a positive rotatory strength (eqn. 5). The high energy part of the circular

dichroism is positive, and thus assigned to the $\Psi_0 \rightarrow \Psi_+$ transition. This means that the angles φ_A and φ_B in eqn. 6 are relatively large as indeed is demanded by the geometry of the molecule and further required by the bulkiness of the methyl groups.
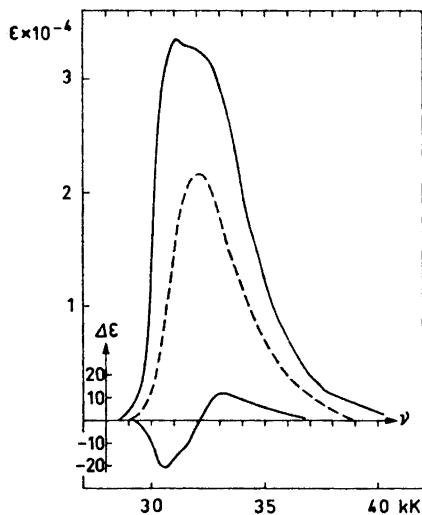

Fig. 1. Molar absorption of polam(acacH) (- - - - - -) and molar absorption and circular dichroism of R-chxn(acacH)$_2$.
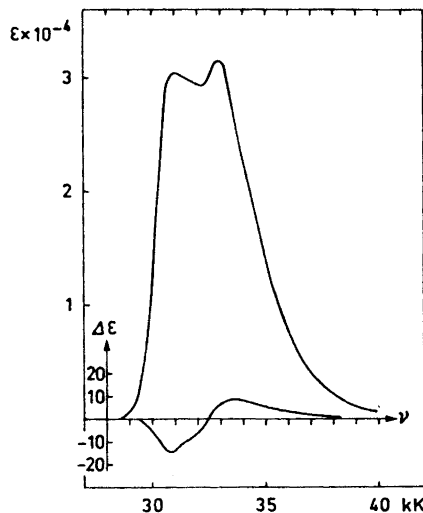
Fig. 2. Molar absorption and circular dichroism of R-pn(acacH)$_2$.

Fig. 2 shows the absorption and circular dichroism spectra for R-pn(acacH)$_2$ There is a pronounced similarity between the spectra of this compound and those of R-chxn(acacH)$_2$ and therefore, the structures are probably similar. However, pn(acacH)$_2$ may be much more flexible. Since the exciton splitting is so large for this molecule that two distinct absorption maxima appear, the flexibility apparently causes the two conjugated parts to approach each other. Attempts to reproduce dimer spectra from linear combinations of two displaced absorption curves of polam(acacH) have not led to completely satisfactory results. This indicates that the coupling between the chromophores in, *e.g.*, pn(acacH)$_2$ is not at the strong coupling limit. The influence of the nuclear vibration on the observed spectra may be complicated, but eqns. 2 and 4 will still hold. Therefore one can, admittedly on a qualitative basis, still draw conclusions about the geometry. Thus structure II displays all the information obtained, and it is evident that the *syn* conformation which is predominant is that which has the methyl substituent *anti* to the Schiff base formed from the 1-amino group.

The absorption and circular dichroism spectra of the analogous derivatives from en and pn with formylcamphor (structure III) seem much more likely to result from strong couplings because ΔE here is 3 kK. In Fig. 3 are given the spectra of R-pn(fmcH)$_2$; en(fmcH)$_2$ gives nearly identical spectra. The
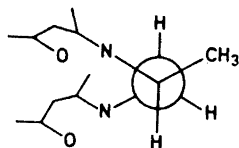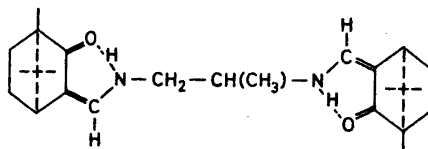
II III

explanation of this must partly be that the chromophores are — unexpectedly — closer to each other. It is interesting that the asymmetry of the camphor group determines the absolute configuration of the conjugated parts both in en(fmcH)$_2$ and in R-pn(fmcH)$_2$.
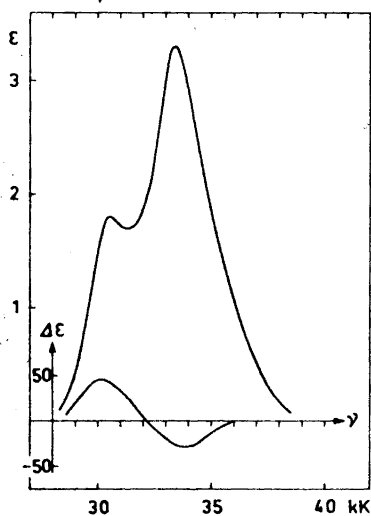

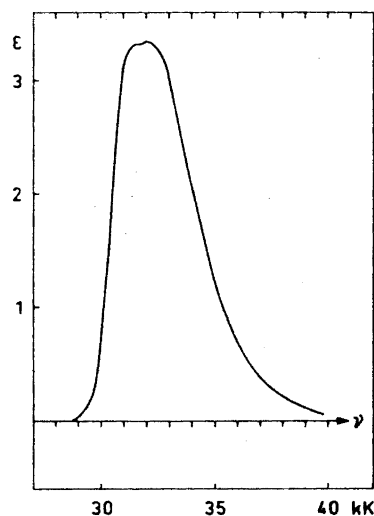*Fig. 3.* Molar absorption and circular dichroism of R-pn(fmcH)$_2$.

Fig. 4. Molar absorption of tn(acacH)$_2$.

From the circular dichroism measurements until now only the signs of the rotatory strengths have been used. It is expected that the two circular dichroism bands of opposite signs under the absorption band partly cancel. For en(fmcH)$_2$ the energy splitting is 3 kK or so large that the cancellation may be unimportant. In this case the experimental $R_- = 50 \times 10^{-24}$ cm^{-1}cm^3 is of reasonable size compared to that calculated theoretically (eqn. 5) $R_- = 120 \times 10^{-24}$ r cosα cm^{-1} cm^3, where α is the angle between the vectors $(P_A \times P_B)$ and R_B and r is half the separation in Å between the chromophores ($r \sim 1.5 - 2$ Å from eqn. 6).

The results show quite unambiguously that the large conjugated groups are close to each other in these dimers in spite of the possibility for a greater separation. The reason for this apparent anomaly may be dipole-dipole attrac-

tion between the two polar groups. Acetylacetone has the rather large dipole moment of 3 D [14] and a similar value is probable for a monomer such as the Schiff base of methylamine and acacH. The dipole moment of the Schiff base of tetramethylenediamine and two acetylacetones is 3.93 D or $ca.$ 2 D per monomer.[15] en(acacH)$_2$ and pn(acacH)$_2$ have the much reduced dipole moments of 3.16 and 2.98 D, respectively.[16] These observations are explained satisfactorily by the stereochemical arrangements proposed here. When there are more than two methylene groups in the bridge, the two conjugated groups do not approach each other significantly as shown by the high dipole moment for the compound with four methylene groups [15] and the very small splitting of the absorption band in tn(acacH)$_2$ with three methylene groups (Fig. 4). The difference between the dipole moments of en(acacH)$_2$ and pn(acacH)$_2$ is caused indirectly by the methyl group on the bridge which presses the two π systems together and produces a high barrier for the rotation around the C—C bond of the bridge. The dipole moment of 3 D for a monomer can explain a stabilization of the *syn* rotamer over the *anti* rotamer by some 5—10 kcal/mole.

CONCLUSION

From the spectral results described in this paper and the use of exciton theory a description of the molecular conformation in solution of some dimeric Schiff bases has been obtained. The experimental energy splittings and intensity ratios which are of importance for the interpretations with exciton theory are measured only with great uncertainty. In spite of this a rather detailed picture of the stereochemistry has emerged. It has been demonstrated that these results are in perfect agreement with values for electric dipole moments of a series of dimeric Schiff bases with variable separation.

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