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DETERMINATION OF THE STEREOCHEMISTRY OF CONDENSATION PRODUCTS BETWEEN α,β-DIAMINES AND α,γ-DIOXO COMPOUNDS BY CIRCULAR DICHROISM, ^{1}H NMR AND X-RAY DIFFRACTION

N. BERNTH and E. LARSEN*
Chemistry Department I, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

and

S. LARSEN
Chemistry Department IV, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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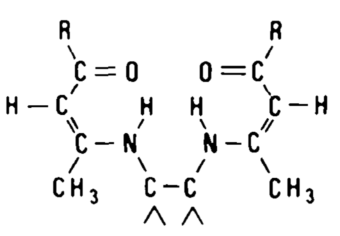
Abstract—The absolute configuration of molecules containing two chromophores of the type -NH–C=C–C=O bridged by –Č–Č– have been studied in solution by UV absorption and circular dichroism. The spectra have been simulated by means of component curves shaped as skew gaussians. The data have been interpreted by means of exciton theory for coupled chromophores to give information about the relative orientation of the chromophores. The result is compared with the result of an X-ray structure determination of *N,N'-bis*(4-oxo-2-penten-2-yl)-R-1,2-diaminopropane.

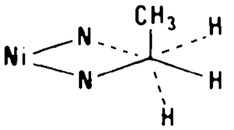
Circular dichroism (CD) has for some time been used to obtain information about the secondary structure of proteins in solution. The basis for such analyses is a description of the protein CD as a sum of CD components from the various structural types for a polypeptide each of which being a sum of at least two exciton components of the $\pi \rightarrow \pi^*$ transitions and a CD component from the $n \rightarrow \pi^*$ manifold of transitions. There is no general agreement of how to do the analysis or to the evaluation of the quality of the analysis.[1-3] This is partly a consequence of the complexity of the problem involving some one hundred interacting peptides and for some kinds of analyses the results may be influenced by the additional assumption that each absorption or CD component is approximated by a Gaussian shaped curve.[4] In this paper we discuss a simple case where two chromophores couple to give two exciton split $\pi \rightarrow \pi^*$ transitions at nearly the same energy as where an $n \rightarrow \pi^*$ transition is found. The molecules are dimeric of the type



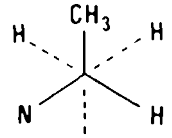
R = CH$_3$, CF$_3$

and their stereochemistry has formerly been studied by ^{1}H NMR, UV absorption and CD.[5,6] The obtained results have lead to a qualitative description of the structure in solution showing that the nitrogen atoms are *gauche* in the dimeric molecule derived from, e.g. ethylenediamine. When the bridge contains a chiral carbon atom as in molecules derived from R-1,2-propanediamine it has further been possible to assign the absolute configuration of the *gauche* arrangement.[5] The combined information in the absorption spectra of R-pn(acacH)$_2$* and polam(acacH) and in the CD spectrum of the former compound interpreted by means of exciton theory should be sufficient for a very detailed determination of the relative orientation of the two halves of the dimeric molecule. We shall show that assuming a certain band shape this is only in part possible. Unfortunately, there is no other method available providing an independent check of the structural results obtained for molecules in solution. Instead we have used X-ray diffraction techniques to determine the crystal structure of R-pn(acacH)$_2$. The structure in solution could very well be different since the molecule should have rotational freedom in the N–C and C–C bonds of the diamine. However, we shall show that the spectroscopic results are best understood if the molecular structure in solution is the same as in the crystalline state and if it possesses a high degree of rigidity.

NMR results. An earlier investigation of the ^{1}H NMR of pn(acacH)$_2$ and its nickel(II) complex concluded that the methyl group on the ethylene bridge in [Ni pn(acac)$_2$] is an axial substituent on the five-membered chelate ring I.[6] The free ligand was postulated to be in the other *gauche* conformation II.[6]



I



II

A determination of the crystal structure of the copper(II) complex with this ligand revealed that the conformation is I,[7] and the present X-ray investigation of the

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*This group of molecules has often been used as ligands for transition metal ions and abbreviations composed by a symbol for the amine (en = 1,2-ethanediamine, R-pn = R-1,2-propanediamine, polam = 2-propanol-1-amine) and the diketone (acacH = acetylacetone, tfacacH = 1,1,1-trifluoro-2,4-pentanedion) are in common use.

free ligand proves the existence of II in the crystalline state. It would be desirable to apply ^{1}H NMR through a Karplus[8] equation for the coupling constants for the protons on the bridge to determine the dihedral angles of II. This would quantitatively show this structural feature in solution. However, the influence of the extended π systems makes such an application very doubtful and it is therefore only possible to reach the crude result depicted as structure II.

The two compounds pn(acacH)$_2$ and pn(tfacacH)$_2$ have identical coupling constants (given in Ref. 7) for the protons on the bridge and we thus infer that the two compounds have identical conformation in solution and that it is close to the one found by X-ray crystallography.

Circular dichroism study

The CD and absorption spectra of R-pn(acacH)$_2$ and R-pn(tfacacH)$_2$ are shown in Fig. 1. The absorption of R-pn(acacH)$_2$ is typical for an exciton coupled dimeric molecule. The splitting is a measure of the distance between the center of the two transition moments located in each ketoenamin and approximately parallel to the line connecting N and O through the relationship

$$\Delta E = 2(\mathbf{P}_A\mathbf{P}_B/r_{AB}^3 - 3(\mathbf{P}_A\mathbf{r}_{AB})(\mathbf{P}_B\mathbf{r}_{AB})/r_{AB}^5),$$

where $\mathbf{P}_A$, $\mathbf{P}_B$ are the two local electric transition moments and $\mathbf{r}_{AB}$ is the vector connecting the center of gravity for the two P vectors. The numerical value for $\mathbf{P}_A{}^2 = \mathbf{P}_B{}^2$ is the transition dipole strength D of a monomeric molecule such as the condensation product between methylamine and acetylacetone. Assuming a twofold axis of symmetry in the dimeric molecule as indicated from the ^{1}H NMR and also from the X-ray structure the above expression contains information about the angle θ between $\mathbf{P}_A$ and $\mathbf{P}_B$, the angle φ between $\mathbf{P}_{A,B}$ and $\mathbf{r}_{AB}$ and the distance r_{AB}. The resulting in-phase(+) and out-of-phase(−) transitions of the molecules with two chromophores have an intensity ratio $D-/D+ = \tan^2(\theta/2)$, where θ is the angle between the chromophores. When the dimeric molecule is chiral the rotatory strengths R_+ and R_- give geometric information through $R\pm = \mp\pi E\pm(\mathbf{P}_A\times\mathbf{P}_B)\mathbf{R}_B$ where $E\pm$ are the component excitation energies and $\mathbf{R}_B$ is the vector connecting the chromophoric center of gravity with the center of $\mathbf{P}_B$. Experimentally a transition dipole strength of an absorption band is measured as an integral over the band:

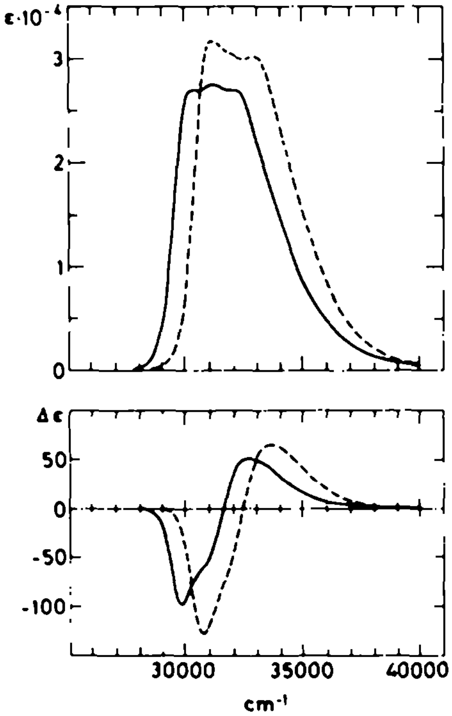

Fig. 1. Absorption and circular dichroism spectra for R-pn(acacH)$_2$ (-----) and for R-pn(tfacacH)$_2$ (——).

$$D = 91.8\times 10^{-40}\int\frac{\epsilon}{\nu}\,d\nu\ \text{erg cm}^3$$
$$= 46.2\times 10^{-24}\int\frac{\epsilon}{\nu}\,d\nu\ \text{cm}^{-1}\,\text{cm}^3$$

and similarly the rotatory strength is obtained from

$$R = \frac{91.8\times 10^{-40}}{4}\int\frac{\Delta\epsilon}{\nu}\,d\nu\ \text{erg cm}^3$$
$$= 11.55\times 10^{-24}\int\frac{\Delta\epsilon}{\nu}\,d\nu\ \text{cm}^{-1}\,\text{cm}^3,$$

where the integration is over the CD band. Thus in principle absorption and circular dichroism spectra of chiral, dimeric chromophores can give detailed information about the distance and the relative orientation of the two parts of the total chromophore. However, only in favourable cases where additional information about the relative structure is present or where the experimental curves are yielding especially good information is it possible to draw conclusive information about the structure. The main reason for this pessimistic statement is that ΔE most often is small relative to the bandwidths and so the determination of D_- and D_+ is ambiguous. The rotatory strengths R_+ and R_- have opposite signs but they should have the same numerical magnitude. The experimental CD curve will be a result of a sum of two CD components which partly cancel. The degree of cancellation and thus the magnitude of $R_\pm$ is impossible to estimate from the experimental curve alone. However, by means of simultaneous simulation of absorption and CD spectra it may be possible to derive at reliable estimates for D_-/D_+, $R_\pm$, and ΔE and in this way describe the structure in solution. This proposition is investigated in the following section.

Simulation of spectra. To test the above discussed relationships we have simulated absorption and CD spectra of R-pn(acacH)$_2$ and R-pn(tfacacH)$_2$. The absorption spectrum of the latter compound has an unusual appearance showing clearly three components. Two of these peaks are assumed to be the exciton components of the $3\pi\to 4\pi$ transition. A third peak could be an $n\to 4\pi$ transition or possibly an unsplit $3\pi\to 4\pi$ band of the molecule in the *anti* conformation. The absorption of the compounds in the crystalline state is similar to the solution spectra and this rules out the latter possibility.

The absorption spectrum of the monomeric polam(acacH) can be described fairly well as a skew gaussian curve

$$\epsilon = \epsilon_0\times[\exp-((\nu_< - \nu_0)^2/d_<{}^2) + \exp-((\nu_> - \nu_0)^2/d_>{}^2)]$$

where ϵ_0 is the maximum absorbancy at ν_0, $d_<$ and $d_>$

are the two half widths at energies less than ($\nu_<$) and higher than ($\nu_>$) that of the maximum, respectively. The experimental spectrum can be simulated even better if a smaller absorption curve representing the n → π* transition is added. However, there is no unique way of constructing the sum curve because the experimental curve is too uncharacteristic. This fact initiated the search for a derivative where the separation between the 3π → 4π and the n → 4π transition is noticeable. For such a spectrum there will be a unique way of simulation, e.g. as a result of a least squares procedure. We have preferred a subjective simulation because the used analytical function has obvious, systematic shortcomings which are not easily compensated for in a minimization procedure. The composite absorption band of the dimeric molecule can then be synthesized as a sum of three skew gaussian curves: $\epsilon(\nu) = \epsilon_-(\nu) + \epsilon_+(\nu) + \epsilon_f(\nu)$ where the suffix f refers to the forbidden n → 4π transition and + − to the in-phase and out-of-phase exciton components. A CD curve was constructed from these functions as $\Delta\epsilon(\nu) = (-\epsilon\ (\nu) + \epsilon_+(\nu) \times D\ /D_+ - \epsilon_f(\nu))(-\epsilon\ (\nu) + \epsilon_+(\nu) + \epsilon_f(\nu)) \times k \times s$ where $D_\pm$ are the electric dipole strengths, k is a weight factor for the CD of the n → 4π transition and s is a scale factor.

Figures 2 and 3 show how it is possible to simulate the absorption spectrum of R-pn(tfacacH)$_2$ by two very different sets of parameters. The simulation shown in Fig. 2 and 4a was made to give a good fit for both absorption and CD and without reference to theoretical predictions. The values for θ, φ and r_{AB} which are deduced from the simulation are reasonable except that θ corresponds to the complement of the value determined by crystallography. Another objection may be the different half widths used for the two exciton components.

Theoretical considerations[9] concerning the vibronic coupling of dimers have not indicated that component absorption bands in a dimer should become much sharper than the band of the monomer and in spite of the good fit we reject the simulations of Figs. 2 and 4a.

With the additional constraint on the simulation that the ε ± curves should have approximately the same half widths as the monomer it is also easy to generate an acceptable absorption curve (Fig. 3) and now θ comes

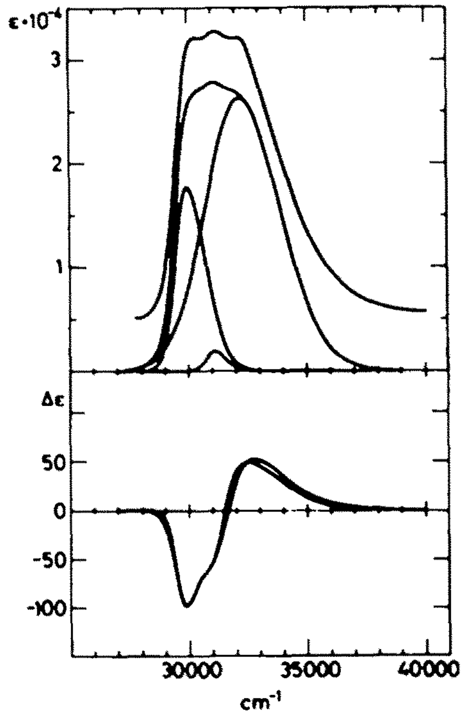

Fig. 2. Simulation of absorption and circular dichroism spectra of R-pn(tfacacH)$_2$ by means of three skew Gaussian curves of different half widths.

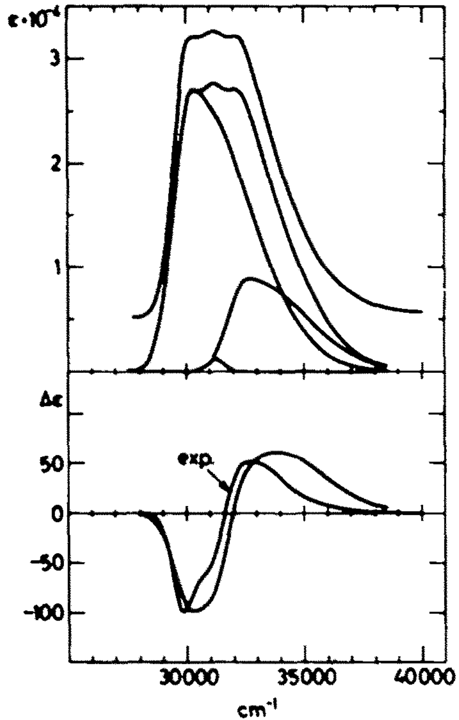

Fig. 3. Simulation of absorption and circular dichroism spectra of R-pn(tfacacH)$_2$ by means of two skew Gaussians shaped as the main absorption of the monomer and a third, much less intense skew Gaussian.

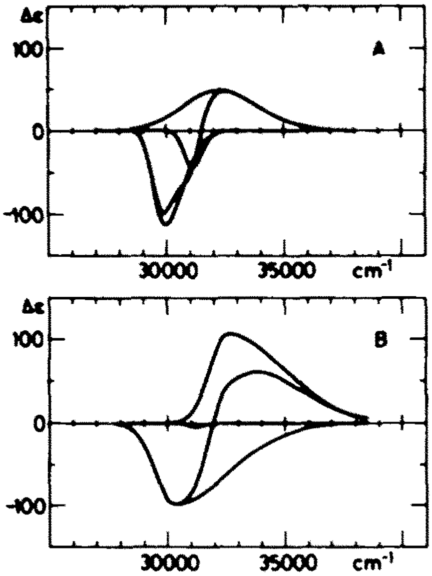

Fig. 4. The component and sum curves in the circular dichroism simulation. In a the intense Gaussians are of different half widths and although the fit (see also Fig. 2) is very good the result is considered bad. In b the Gaussians of Fig. 3 are used.

out right. Instead difficulties are introduced in the simulation of the CD curve where the component CD curves in the simulation are too broad for a good likeness. The problems are serious for the tail of each component. However, in the tail region the vibronic coupling could produce CD contributions of both signs resulting in an apparent shrinking and we therefore find that the simulation is satisfactory (Figs. 3 and 4b). The resulting parameters for simulation are given in Table 1 where also parameters for polam(acacH) and pn(acacH)$_2$ are included. The parameters are very similar and the mere fact that it is possible to do such simulations suggests that the compounds behave as if they have large barriers to rotation.

From the atomic coordinates (*vide infra*) we have calculated a set of vectors and distances of relevance for the CD study. The electric transition dipole moment, **P**, for the $3\pi \rightarrow 4\pi$ transition of the oxoenamine moiety has been approximated by the unit vector connecting N and O of this group. This is not strictly correct since the direction of **P** is only parallel to this vector when the chromophore is symmetric (e.g. the anion of 2,4-pentanedione). Judged from Hückel MO calculations the error is minor. The position of **P** in the plane of the oxoenamine is not defined (but it must of course lie within the dimension of the molecule) and therefore the distance between the P-vectors of each π system is uncertain. However, this choice of **P** connecting N and O produces an energy splitting very close to the one reached by the simulation, see Table 2. The experimental values for the rotatory strengths for the negative and positive CD components are -60×10^{-24} cm^{-1} cm^3 and 48×10^{-24} cm^{-1} cm^3, respectively. From the two unit P-vectors and the experimentally obtained dipole strength for the dimer (2.02×10^{-19} cm^{-1} cm^3) we calculate $R_+ = 102 \times 10^{-24}$ cm^{-1} cm^3. This result is in accord with the simulation of the CD shown in Fig. 4b where nearly half of the rotatory strength of each exciton component cancel. Thus the simulation (Figs. 3 and 4b) is consistent with the structure as we know it is in the crystalline state. The mere fact that it is possible to simulate the absorption of the dimeric molecules with only three components of the

Table 1. Parameters used in the simulation of Figs. 2–4

		ϵ_0	$10^{-3}\nu_0$ cm^{-1}	$d_<$ cm^{-1}	$d_>$ cm^{-1}	$10^{19}D$ cm^{-1}cm^3
I	$\pi \rightarrow \pi^*$	19400	31.75	1100	3400	1.08
	$n \rightarrow \pi^*$	1200	32.50	500	500	0.015
	out-of-phase	17600	29.90	640	1170	0.432
II	$n \rightarrow \pi^*$	1700	31.10	500	600	0.025
	in-phase	26100	32.15	1990	2440	1.46
	out-of-phase	26900	30.25	1050	3400	1.56
III	$n \rightarrow \pi^*$	1200	31.20	400	450	0.013
	in-phase	8800	32.60	1050	3400	0.47
	out-of-phase	30700	31.15	1050	3400	1.73
IV	$n \rightarrow \pi^*$	1200	30.95	400	450	0.015
	in-phase	8800	33.45	1050	3400	0.46

I is for polam(acacH), II as shown in fig. 2, III as shown in fig. 3 and IV is for R-pn(acacH)$_2$.

Table 2. Spectral properties for R-pn(tfacacH)$_2$ in methanol

	Experimental	Calculated
Total D	2.02×10^{-19} cm^{-1}cm^3	2.04×10^{-19} cm^{-1}cm^3 (a)
ΔE	2.35×10^3 cm^{-1}	2.13×10^3 cm^{-1} (b)
θ	126.8° (c)	123° (a)
R_-	-61×10^{-24} cm^{-1}cm^3	-102×10^{-24} cm^{-1}cm^3 (b)

(a) Result of the simulation based on the parameters of table I.

(b) Calculated from (1) using $P_A = P_B = \sqrt{D/2}$, and using the positions of oxygen and nitrogen to define the unit vectors.

(c) Result from the X-ray structure determination letting the position of oxygen and nitrogen define the direction of the vector.

same shape as found for a monomeric molecule suggest that the dimeric ones are of a distinct geometry. This is a surprising result in view of the force field calculations performed by Bresciani-Pahor *et al.*[10] Their force field does not contain electrostatic contributions to the energy function and this may be the reason for the appearance of a number of flat minima at approximately equal energy for en(acacH)$_2$. This result is not in agreement with the absorption spectrum which is very similar to that of pn(acacH)$_2$ and we should therefore expect a similar conformer distribution for the two compounds in solution.

X-ray study. The molecular structure of *N,N'-bis*(4 - oxo - 2 - penten - 2 - yl) - R - 1,2 - diaminopropane is illustrated by the ORTEP drawings in Figs. 5 and 6. For clarity the molecule is shown correctly with only one methyl group on the diaminoethane moiety in spite of the crystal symmetry which implies that the molecule possesses a two-fold axis of symmetry. Figure 5 demonstrates how the two π- systems are related by the two-fold axis. As predicted by the spectroscopic methods the conformation of the molecule is *gauche*. The dihedral angle N–C(6)–C(6')–N' is −65.7°. Figure 6 depicts the molecule almost oriented in a Newman projection along C(6)–C(6').

The bond lengths and bond angles are listed in Table 3 and the results from the calculation of a least squares plane of the ketoenamine are shown in Table 4. From these results it is apparent that the π-system is planar and that the bond lengths show a pronounced conjugation within the system. The hydrogen atoms H(1) and H(3) are in the plane of the π-system with H(1) forming an intramolecular hydrogen bond between O and N(H(1)---O = 1.93 Å, N---O = 2.67 Å). The planes of the π systems of a molecule form an angle of 40°.

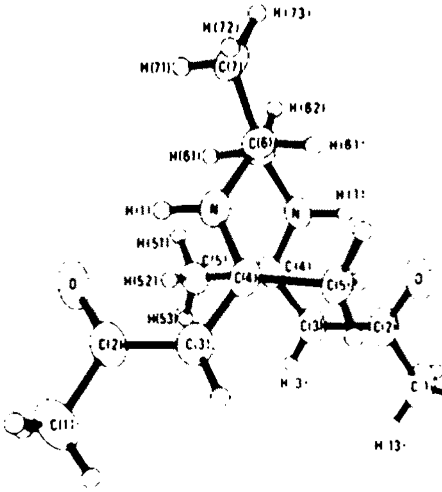

Fig. 6. An ORTEP drawing of R-pn(acacH)$_2$ showing the conformation of the bridging diamine.

The positions of all the hydrogen atoms were clearly located and this crystal structure therefore confirms that the molecule exists as the ketoenamine tautomer and not as a Schiff base.

The overall structure of R-pn(acacH)$_2$ is very similar to that of en(acacH)$_2$.[10] The latter molecule is known to possess a two-fold axis of symmetry in solution[11] but it does not crystallize with the molecule on the site of a two-fold axis. However, considering the standard deviations en(acacH)$_2$ has an effective two-fold symmetry also in the crystal. A difference in the bond distances C(2)–C(3)(1.44 Å) and C(3)–C(4)(1.39 Å) was observed in the structure of en(acacH)$_2$. This is even more pronounced in the structure of R-pn(acacH)$_2$ where C(2)–C(3) = 1.434 Å and C(3)–C(4) = 1.376 Å. This variation does not seem to occur in an amine condensation product with the thio analogue of acetylacetone where the corresponding bond lengths are reported to be almost identical.[12]

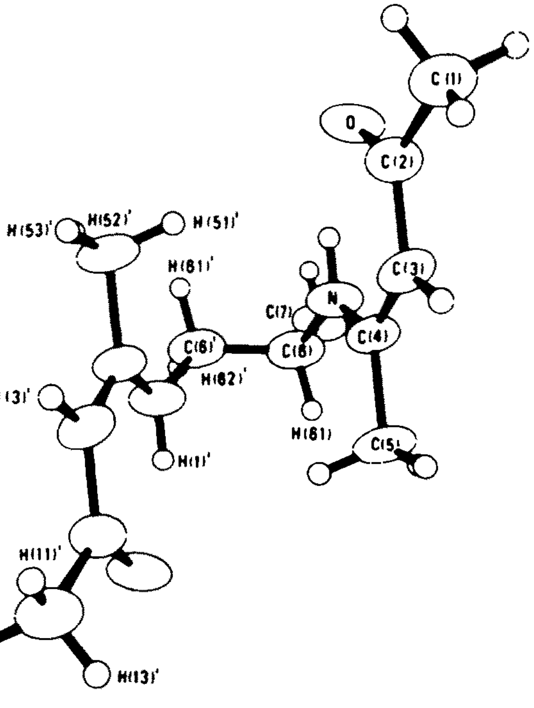

Fig. 5. An ORTEP drawing of R-pn(acacH)$_2$ showing the two-fold symmetry relating to the two π-systems.

Table 3. Crystal data

$C_{13}H_{22}N_2O_2$; M = 238.33; P $3_2$21 from systematic absences

d_{obs} = 1.05 g/cm^3; Z = 3; d_{cal} = 1.08 g/cm^3

F(000) = 390; μ(MoKα) = 0.54 cm^{-1} (23 °C)

	296 K	90 K
a	8.129(8) Å	7.959(6) Å
c	19.23(3) Å	19.109(15) Å
v	1100.7 Å^3	1048.2 Å^3
scan rate	0.5° min^{-1}	2° min^{-1}
A	1.0°	1.0°
B	1.2°	1.4°
$2\theta_{max}$	43°	55°
Unique reflections	554	1000
Observed reflections	326	806

Table 4. Fractional coordinates* with estimated standard deviations in unit of the last digits in parentheses

Atom	x	y	z	Population
C(1)	-0.5676(5)	-0.2570(8)	0.32608(17)	1.0
C(2)	-0.3855(5)	-0.1313(6)	0.36720(13)	1.0
C(3)	-0.4011(4)	-0.1122(5)	0.44117(13)	1.0
C(4)	-0.2462(4)	0.0030(4)	0.48378(12)	1.0
C(5)	-0.2780(5)	0.0056(5)	0.56179(13)	1.0
C(6)	0.1109(5)	0.2213(5)	0.49817(15)	1.0
C(7)	0.2458(12)	0.4178(10)	0.4734(3)	0.5
N	-0.0680(4)	0.1127(4)	0.45827(11)	1.0
O	-0.2283(3)	-0.0451(5)	0.33530(9)	1.0
H(1)	-0.060(8)	0.100(8)	0.411(3)	1.0
H(3)	-0.526(9)	-0.187(8)	0.461(3)	1.0
H(11)	-0.609(8)	-0.172(9)	0.299(3)	1.0
H(12)	-0.678(9)	-0.353(8)	0.354(3)	1.0
H(13)	-0.543(8)	-0.325(9)	0.292(3)	1.0
H(51)	-0.215(9)	-0.056(9)	0.586(3)	1.0
H(52)	-0.415(8)	-0.066(9)	0.572(3)	1.0
H(53)	-0.215(9)	0.154(9)	0.579(3)	1.0
H(61)	0.079(8)	0.234(8)	0.546(3)	1.0
H(62)	0.192	0.349	0.481	0.5
H(71)	0.183(18)	0.495(18)	0.471(6)	0.5
H(72)	0.255(17)	0.394(16)	0.429(6)	0.5
H(73)	0.390(17)	0.500(17)	0.498(6)	0.5

The coordinates for the other half of the molecule can be generated by the symmetry operation (y,x, 1.0-z).

Table 5. Bond lengths (Å) and bond angles (deg) with estimated standard deviations in parentheses

C(1) - C(2)	1.507(5)	C(1) - C(2) - O	118.6(3)
C(2) - C(3)	1.434(4)	C(1), - C(2) - C(3)	118.6(3)
C(2) - O	1.245(4)	C(3) - C(2) - O	122.7(3)
C(3) - C(4)	1.376(4)	C(2) - C(3) - C(4)	123.9(3)
C(4) - C(5)	1.514(4)	C(3) - C(4) - C(5)	119.5(2)
C(4) - N	1.332(4)	C(5) - C(4) - N	118.8(2)
N - C(6)	1.458(4)	C(3) - C(4) - N	121.7(2)
C(6) - C(7)	1.465(7)	C(4) - N - C(6)	127.0(2)
C(6) - C^{1}(6)	1.525(7)	N - C(6) - C(7)	116.2(4)
C(1) - H(11)	1.02(8)	N - C(6) - C(6)^{1}	110.8(3)
C(1) - H(12)	0.99(5)	C(7) - C(6) - C(6)^{1}	107.8(5)
C(1) - H(13)	0.93(7)	C(2) - C(3) - H(3)	117(3)
C(3) - H(3)	0.95(6)	C(4) - C(3) - H(3)	119(3)
C(5) - H(51)	0.97(8)	C(4) - N - H(1)	114(3)
C(5) - H(52)	0.96(6)	C(6) - N - H(1)	119(4)
C(5) - H(53)	1.08(6)	N - C(6) - H(61)	109(3)
N - H(1)	0.91(6)	C(7) - C(6) - H(61)	106(3)
C(6) - H(61)	0.96(6)	C(6)^{1} - C(6) - H(61)	106(5)
C(7) - H(71)	0.97(17)		
C(7) - H(72)	0.88(11)		
C(7) - H(73)	1.10(11)		

Table 6. Distances (Å) from a least squares plane. The atoms marked with * are those used to define the plane

Atom		Atom	
C(1)	0.085	N*	0.014
C(2)*	0.011	C(6)	-0.171
C(3)*	0.005	C(7)	0.747
C(4)*	-0.018	H(3)	-0.006
C(5)	-0.083	H(1)	0.027
O*	-0.013		

EXPERIMENTAL

1,2-propanediamine was resolved by precipitation of the *d*-tartrates[13] and the condensation products were prepared according to the known simple procedures.[5,14] The identity of the compounds were established from chemical analyses and ^{1}H NMR spectroscopy.

Spectral measurements. The UV spectra were recorded on a Cary 118 spectrophotometer and the CD spectra were measured on a Roussell-Juan Dichrograph IIIS interfaced with a Tektronix 4051 minicomputer. ^{1}H NMR was obtained by a Bruker HX-270 spectrometer.

X-ray diffraction

Crystal characteristics. N,N' - bis(4 - oxo - 2 - penten - 2 - yl) - R - 1,2 - diaminopropane was recrystallized from diethylether to obtain crystals suited for X-ray diffraction work. The crystals are transparent, prismatic needles elongated in the direction of the *c*-axis. Preliminary Weissenberg and precession photographs showed that the crystals are trigonal. The symmetry of the diffraction pattern is $\bar{3}$m and the space group was determined from the systematically absent reflections to be one of the enantiomer pair P 3_121 or P 3_221. The density of the crystals was measured at 23° by flotation in a saturated aqueous solution of the compound. The crystal data is given in Table 3.

Data collection and data reduction. Two sets of data were collected for this compound. Initially the intensities were measured at 23° but as the resolution is very limited and the thermal diffuse scattering is large at this temperature another set of data was collected at 90 K. In both cases the measurements were performed with a Picker FACS-1 diffractometer utilizing Mo*K*α radiation from a highly mosaic graphite crystal. A modified Enraf-Nonius low-temperature device was used to cool the crystal. The temperature was kept constant within 0.5 K during the experiment.

The setting angles for 27 (296 K) and 11 (90 K) reflections were determined automatically on the diffractometer. These measurements were used in a least squares refinement of the orientation matrix and the cell constants. The data were measured by operating the diffractometer in a $\theta - 2\theta$ scan mode. The scan range was asymmetrical from $2\theta_1 = 2\theta_0 - A - 0.346 \tan \theta$ to $2\theta_2 = 2\theta_0 + B + 0.346 \tan \theta$, where $2\theta_0$ is the calculated peak position. The constants A and B are listed with other experimental conditions in Table 3. Background counts were made at each end of the scan range for 20 s. Three standard reflections were measured after every 30 (296 K) or 50 (50 K) reflections. The intensities of these reflections remained constant at 90 K but decreased with the exposure time at 296 K. The room temperature data were corrected for this deterioration using a rescale function linear in the exposure time. The reflections were measured in the hemisphere $l \geq 0$. The data set was corrected for Lorentz and polarization effects and the symmetry related reflections were averaged.

The Laue symmetry $\bar{3}$m implies that the molecule is on a twofold axis of symmetry and thus forces the crystal structure to be disordered in a regular way. To test whether the visually determined Laue symmetry is correct the data reduction was also performed assuming the Laue symmetry $\bar{3}$ corresponding to a ordered structure. A residual

$$R = \sum_s \sum_i \left| F_i(\bar{h})^2 - F_s(\bar{h})^2 \right| \Big/ \sum \sum F_i(\bar{h})^2$$

was calculated for each of the data reductions. $|F_s(\bar{h})|^2$ represents the averaged and $|F_i(\bar{h})|^2$ the individual measurements of the squared structure amplitudes. The residuals were virtually identical for the data reductions in $\bar{3}$m and $\bar{3}$, R(296 K) = 0.08, R(90 K) = 0.03, confirming the visually estimated Laue symmetry.

The reflections were considered observed if $I \geq 2\sigma(I)$ where $\sigma(I)$ is the standard deviation calculated from counting statistics.

Structure determination and refinement. The structure was solved by direct methods from the room temperature data using the program assembly MULTAN. A standard run showed all the non-hydrogen atoms in the structure except the methyl carbon of the R-propylene moiety. The position of this atom was found from a difference Fourier. The structure was refined by the method of least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ using the space group P $3_2$21 in order to obtain the correct, known absolute configuration.[7] For the room temperature data the contributions from the hydrogen atoms were included but not refined and anisotropic temperature factors were introduced for the methyl carbon atoms. Despite these efforts the conventional R-value converged at 0.12 and the standard deviations were very large. In the refinement of the low temperature data anisotropic temperature factors were gradually introduced for all the non-hydrogen atoms. The positions of all the hydrogen atoms even the half populated ones were determined unambiguously from a difference Fourier. The hydrogen atoms were given a fixed isotropic temperature factor, $\exp(-0.79 \sin^2 \theta/\lambda^2)$, but their positional parameters were included in the refinement. However, the parameters for the half populated hydrogen atom, H(62), refined to physical unrealistic values and they were correlated with the parameters for the methyl carbon atom. In the final cycles of least squares refinement the positional parameters were fixed at the idealized calculated values. There was no indication in the difference Fourier that the molecular symmetry deviates from C_2. So the population factor for the appropriate atoms was fixed to 0.5. During the final cycles of the least squares refinement the weights used follow the expression $w^{-1} = 1.0 + 0.6\sigma(F)^2 - 0.044F + 0.0035F^2 - 1.3 \sin \theta/\lambda$. In the last cycle the maximum shift of parameters was 0.65 σ for one of the partly populated H atoms and the final residuals were R = 0.044 and R_w = 0.060.

The atom scattering factors used in the calculations were those of Cromer and Mann[15] except for hydrogen where the values of Stewart *et al.*[16] were used. During the computations the following computer programs were employed. The VANDERBILT system, MULTAN, the X-RAY system, and ORTEP II.[17-20]

The results reported here are those derived from the data collected at 90 K as these obviously are the most reliable. The final positional parameters are shown in Table 4. The anisotropic thermal parameters and lists of observed and calculated structure amplitudes are available from the authors on request.

Note addded in proof. Computer resolution of the overlapping electronic absorption bands by means of a least squares procedure for log-normal curves have been performed on Tektronix 4051 inspired by a recent paper.[21] These computations lead to the same conclusions as those reported here.

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