which is included in S.[6,7]) Reading is accomplished in these materials in the IR with the UV light source turned off; i.e., no photochemistry occurs during the reading process. Therefore no reduction of the recorded diffraction efficiency occurs; the hologram is self-developing. RNO in p-(alkyl-CAc) are one-photon, two-level materials, which need a development process to allow nondestructive reading. However, such a development is easily accomplished by sublimating the residual RNO from the polymer. This works excellently because of the high vapor pressure of the RNO.

Concerning the demand for nondestructive reading, two-photon materials are more advantageous compared to one-photon materials. But due to the fact that a two-photon process in general shows a smaller cross section than a one-photon process, both mechanisms should be kept in mind for developing new photopolymer systems with high photosensitivity in the near-IR. However, from our results the main question seems to be whether a considerable photomechanical effect can be induced in the polymer matrix. Only this enhancement effect may provide the high photosensitivity required for an efficient holographic recording material, as was demonstrated here with RNO/p-(alkyl-CAc).

5. Conclusion

A new class of near-IR-sensitive organic materials for holographic recording was found, consisting of tertiary nitrosoalkanes (RNO) as the photoreactive component and poly(alkyl α-cyanoacrylates) (p-(alkyl-CAc)) as the polymer matrix. After absorption of one photon at wavelengths up to 799 nm a homolytic dissociation of the C–N bond occurs in RNO, giving alkyl and nitric oxide radicals, which subsequently react with the polymer matrix. The last reaction step was found to be activation energy controlled. The quantum yield of the photoreaction of the RNO in the solid polymer matrix is relatively low compared to the quantum yield in liquid solution, probably because of the low mobility of the reaction partners and a high recombination rate of the primary produced radicals. Activation energies and quantum yields depend strongly on the glass transition temperature of the polymer, i.e., the rigidity of the framework of the polymer host.

The photochemical reaction of the RNO is accompanied by a considerable photomechanical effect leading to an expansion of the polymer matrix. Accordingly, a density decrease and thus a high change of refractive index are induced. Therefore, RNO in p-(alkyl-CAc) forms an excellent refractive index material with spectral sensitivity in the near-IR for various applications, e.g., integrated optics and holographic recording. The change of the refractive index due to the photomechanical effect is the dominant contribution to the overall change of refractive index and is found to depend strongly on the state of polymerization and composition of the polymer. The near-IR holographic sensitivities of the new materials were determined and were found to be about 3 orders of magnitude higher than the sensitivities of the two other known near-IR-sensitive organic holographic recording materials.[6,7] It was indeed possible to record holograms in RNO/p-(EtCAc) with a GaAlAs laser.

Acknowledgment. We are very grateful to the VW-Stiftung and the Fonds der Chemischen Industrie for support of this work. The helpful assistance of M. Piatkowski and the excellent electronic support of H. Horbach are gratefully acknowledged.

Chiral β-Cyclocitral Schiff Bases: A Combined Spectroscopic and Theoretical Approach to a Twisted Enimine Structure

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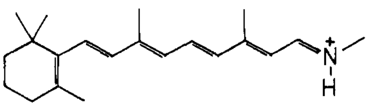
Abstract: UV and CD spectra of eight β-cyclocitral Schiff bases rendered chiral by virtue of an asymmetrically substituted imine part have been measured and rationalized on the basis of force-field (MMP2) and quantum-mechanical (CNDO) calculations. They show the compounds to exist as a temperature- and solvent-dependent mixture of highly twisted s-cis and close to planar, but less stable s-trans conformers. Both $\pi\pi^*$ and $n\pi^*$ absorptions are unambiguously assigned, the former in the UV spectra and the latter in the CD spectra; however, only the sign of the $n\pi^*$ band correlates with the absolute conformation of the diene, being plus for M and minus for P helicity.

I. Introduction

Photochemically induced isomerization processes and conformational changes of protein-bound retinal play a central role in the primary reaction sequences that eventually result in a visual signal.[1] These changes involve mainly the open-chain chromophore of the protonated retinal Schiff base 1; however, for detailed studies concerning, e.g., protein–chromophore interaction[2] or the peculiar spectral shifts observed for visual pigments,[3] the structure of the whole molecule, including the terminal β-ionone ring, has to be taken into account.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Because of severe steric interaction of the hydrogens on C7 and C8 with the methyl groups on C1 and C5, the preferred coplanar arrangement of the endocyclic double bond with the polyene chain is not possible. Instead, the molecule adopts a conformation derived from a twisted s-cis or s-trans arrangement along the C6–C7 linkage. In the solid state, *all-trans*- and 11-*cis*-retinal

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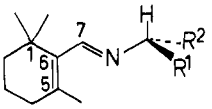
are found to be twisted by 58.3 and 41.4°, respectively, from s-cis.[4] According to ^{1}H NMR studies including NOE,[5,6] a highly twisted s-cis ring–chain conformation predominates in solution as well, in agreement with theoretical calculations.[7]

The twist about the ring–chain junction renders the retinal chromophore inherently chiral; in a chiral environment the enantiomers could be distinguished, e.g., by chiroptical methods. It appears, however, that the CD spectra reported for visual pigments[8] (in which the native protein provides the chiral environment) or for Schiff bases obtained by condensing retinal with chiral amines[9] are not sufficient to differentiate between the two mechanisms by which CD absorption can be envisaged to occur, namely, either by the inherent chirality of the chromophore alluded to above or by the coupling of the retinal transition moments with transition moments located in the protein environment or in the amine part of the Schiff base. The latter effect does not depend on any particular conformation of the retinal chromophore and could in principle even be observed with a planar π system.

We have shown recently[10] the existence of twisted ring–chain conformations in β-cyclocitral Schiff bases, using CD spectroscopy.



These molecules may be looked at as radically shortened retinal analogues that retain, except for substitution of nitrogen for CH at the 8-position, the essential steric features about the C6–C7 bond. Only chromophorically inactive substituents R^1 and R^2 were employed to make sure that any strong CD observed reflected the inherent chirality of the diene chromophore. We have extended this study now to a number of different β-cyclocitral Schiff bases; also, we have performed force-field and quantum-mechanical calculations on these systems.

II. Experimental Section

Materials. β-Cyclocitral was a gift from BASF. (*S*)-(+)- and (*R*)-(−)-2-aminobutane were purchased from Norse, and (*S*)-(+)-2-amino-1-propanol and (*S*)-(+)- and (*R*)-(−)-2-amino-1-butanol were obtained from Fluka. (*R*)-2-Aminopentane and (*R*)-2-amino-3-methylbutane were resolved from the racemates with L-tartaric acid (specific rotations $[\alpha]_D^{25}$ = −5.95 and −3.35° (neat), respectively). (*R*)-(−)-2-Amino-2-methyl-1-butanol was obtained by reduction of D-valin. Solvents used (isopentane, Rigisolve (2,2-dimethylbutane/*n*-pentane, 8:3), and methanol/ethanol, 4:1) were of spectrograde quality.

Preparation of Schiff Bases. Condensation of β-cyclocitral with an excess of amine was achieved depending on reactivity and solubility of the reactants: **2** and **3** by refluxing in *n*-hexane over molecular sieves (3 Å) for 3 h under an inert atmosphere; **4** and **5** by stirring in dry ether at room temperature over molecular sieves for 24 h; 6, **7**, and **8** by refluxing in absolute benzene with separation of water for 3 h; **9** by refluxing in ether for 5 h. After the solvent and excess amine were stripped off, the products were analyzed. For UV and especially CD measurements, extra care was taken to completely remove any free (chiral) amine. For this, all Schiff bases were purified via HPLC on a polar silica gel column (Si-60, 5 μm, length 250 mm, width 4 mm) with *n*-hexane/ether (27:5) as eluant (UV detection at 240 nm).

Table I. Chiral Schiff Bases Used in This Study

compd	R^1	R^2	amine employed
2	CH_3	CH_2CH_3	(*S*)-2-aminobutane
3	CH_2CH_3	CH_3	(*R*)-2-aminobutane
4	*n*-C_3H_7	CH_3	(*R*)-2-aminopentane
5	$CH(CH_3)_2$	CH_3	(*R*)-2-amino-3-methylbutane
6	CH_3	CH_2OH	(*S*)-2-amino-1-propanol
7	CH_2CH_3	CH_2OH	(*S*)-2-amino-1-butanol
8	CH_2OH	CH_2CH_3	(*R*)-2-amino-1-butanol
9	CH_2OH	$CH(CH_3)_2$	(*R*)-2-amino-3-methyl-1-butanol

Table II. Nonstandard MMP2 Parameters Used in This Study

Stretching Parameters

bond type	k_s, mdyn pm^{-1}	l_0, pm
$C(sp^2){=}N(sp^2)$	0.102, 0.046[a]	126.5, 0.156[a]
$C(sp^3)–N(sp^2)$	0.034	141.3

Bending Parameters

angle type	θ_0, deg	k_b, mdyn pm rad^{-2}
$C(sp^3)–C(sp^2)–N(sp^2)$	122.5	50
$C(sp^3)–C(sp^2)–N(sp^2)$	120	46
$H–C(sp^2)–N(sp^2)$	121.5	20
$C(sp^3)–C(sp^3)–N(sp^2)$	109	57
$H–C(sp^3)–N(sp^2)$	109	50
$C(sp^3)–N(sp^2)–C(sp^2)$	117.5	63
$C(sp^2){=}N(sp^2)–H$	110	50
$C(sp^2)–N(sp^2)–LP$[b]	125	50
$LP–N(sp^2)–H$	125	50
$C(sp^3)–N(sp^2)–LP$	124	50

Torsional Parameters[c]

angle type	V_1	V_2	V_3
$H–C(sp^2)–N(sp^2)–H$	0	14.25	0
$H–C(sp^2)–N(sp^2)–LP$	0	14.25	0
$C(sp^3)–C(sp^2)–N(sp^2)–LP$	0	14.25	0
$C(sp^3)–C(sp^2)–N(sp^2)–H$	0.6	14.25	0
$H–C(sp^3)–C(sp^2)–N(sp^2)$	0	0	−0.06
$H–C(sp^3)–N(sp^2)–C(sp^2)$	0	0	−0.24
$C(sp^3)–C(sp^2)–N(sp^2)–C(sp^3)$	0	14.25	0
$H–C(sp^3)–N(sp^2)–LP$	0	0	1.18
$C(sp^2)–C(sp^2)–C(sp^2)–N(sp^2)$	0	15	0
$H–C(sp^2)–C(sp^2)–N(sp^2)$	0	15	0
$C(sp^2)–C(sp^2)–N(sp^2)–H$	0	14.25	0
$C(sp^2)–C(sp^2)–N(sp^2)–LP$	0.6	14.25	0
$C(sp^3)–C(sp^3)–C(sp^3)–N(sp^2)$	0.1	0.4	0.5
$O(sp^3)–C(sp^3)–C(sp^3)–N(sp^2)$	0	0	0
$H–C(sp^3)–C(sp^3)–N(sp^2)$	0	0	0.53
$C(sp^3)–C(sp^2)–C(sp^2)–N(sp^2)$	0	16.25	0
$N(sp^2)–C(sp^3)–C(sp^2)–C(sp^2)$	0	0	0
$C(sp^2)–C(sp^3)–N(sp^2)–C(sp^2)$	0	0	0.3
$C(sp^2)–C(sp^3)–N(sp^2)–LP$	0	0	3.25
$C(sp^3)–C(sp^3)–N(sp^2)–C(sp^2)$	0	0	0.3
$C(sp^3)–C(sp^3)–N(sp^2)–LP$	0	0	3.25
$C(sp^2)–C(sp^2)–N(sp^2)–C(sp^3)$	0	16.25	0

[a] Correction factor for π-part calculation. [b] Lone pair of electrons on nitrogen. [c] Energy in kcal/mol.

Analytical Data. All Schiff bases gave satisfactory elemental analysis and mass spectral data. In the IR, they show strong absorption around 1628 cm^{-1} due to the conjugated C=N bond. The OH absorption of the hydroxy amine Schiff bases is strongly concentration dependent. In CCl_4 at 0.04 mol/L, the free OH band occurs at 3595 cm^{-1}. At higher concentrations, a broad absorption around 3380–3280 develops, indicating the intermolecular formation of strong hydrogen bridges presumably involving nitrogen as acceptor. ^{1}H NMR data agree with the assumed structures. The protons of the *gem*-dimethyl group of **4** in $CDCl_3$ appear as a singlet with δ = 1.12 at room temperature, which splits into a doublet below 233 K (δ = 1.05, 1.07). This splitting occurs only in cyclocitral Schiff bases containing a chiral center, so we attribute it to slow interconversion of diastereomers oppositely twisted about the C6–C7 bond.

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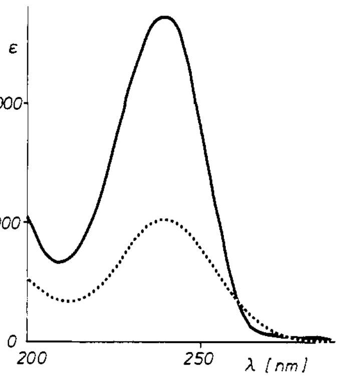

Figure 1. Absorption spectrum of **2** in isopentane (—) and methanol/ethanol (···).

Table III. Extinction Coefficient ε (L mol^{-1} cm^{-1}) at Room Temperature and 240 nm

	isopentane	methanol/ethanol
2, **3**	13 700	5200
4	13 300[a]	5300
5	12 900	5300
6	12 300	5350
7, **8**	11 000	6050
9	10 500	5500

[a] Measured in Rigisolve.

A similar effect has been reported for β-ionole.[11]

Electronic Spectra. UV spectra were obtained on a Perkin-Elmer Lambda 5 spectrophotometer, and CD spectra were obtained on a Jobin-Yvon dichrograph Mark IV with digital data accumulation, both equipped for thermocontrolled low-temperature measurements. All spectra shown are corrected for solvent contraction.

III. Computational Procedures

Molecular mechanics (MM) calculations with Allinger's MMP2 force field[12] were used to obtain molecular geometries. The nonstandard force-field parameters that we needed were derived by adjusting MMP2 results to ab initio and X-ray results on the structures and torsional barriers of small imines. The parameters are listed in Table II. We have found that these parameters yield a very satisfactory description of the preferred imine conformations.[13] For the extensive geometry optimization of **2** and **6**, the torsional potential about the C–N bond was calculated in steps of 15° allowing complete relaxation of all geometric variables without symmetry constraints.

CNDO/S calculations were performed by using the program CNDO, which is part of the MONDO package.[14] Excited states were generated by configuration interaction (CI) between the 200 lowest singly and doubly excited states using a program developed by Hohlneicher and Dick.[15] Rotatory strengths were obtained by calculating electric and magnetic transition moments on the basis of CNDO/S wave functions and the CI matrix.[16] For the electric dipole operator, we used the velocity expression to ensure origin independence of the calculated rotatory strengths.

IV. Results

UV Spectra. In absorption above 200 nm the β-cyclocitral Schiff bases show just one unstructured band with maximum at about 240 nm and intensity that strongly depends on solvent polarity. In Figure 1 the UV spectra of **2** in isopentane and methanol/ethanol are compared showing the significant decrease of extinction in the latter. Similar changes are observed for the other Schiff bases; numerical results are summarized in Table III.

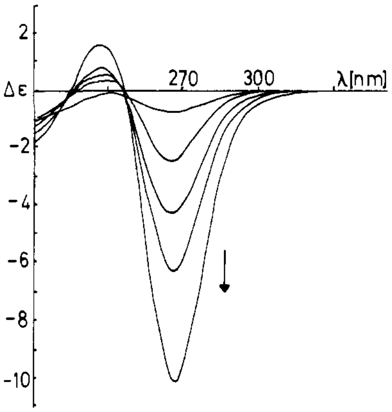

Figure 2. Temperature-dependent CD spectra of **2** in isopentane. The arrow in this figure (as in following ones) always points in the direction of lower temperatures. Curves shown correspond to measurements at 233, 193, 173, 153, and 123 K, respectively.

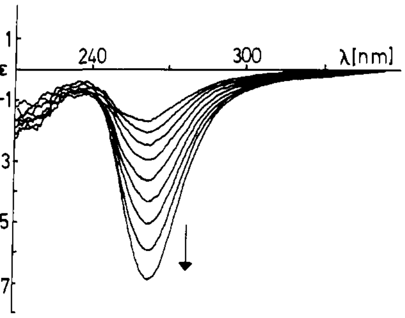

Figure 3. Temperature-dependent CD spectra of **2** in methanol/ethanol. Measurements starting at 283 K were done in 20 K intervals except for the first, which is 30 K.

Table IV. Rotational Strength R (in 10^{-40} cgs) of the 264-nm Band in Methanol/Ethanol

T/K	**2**	**4**	**5**	**7**[a]	**9**[a]
283	−3.9	1.1	0.9	0.9	−0.9
253	−4.6	1.5		2.0	−1.5
233	−6.2				
223		2.6	2.4	3.5	−2.3
213	−7.2				
193	−9.0	3.7	3.3	5.3	−3.4
173	−10.6				
163		4.9		7.3	−4.6
153	−12.6				
143		5.8	6.0		−5.4
133	−14.6			9.9	
123		7.2	7.7		−6.3
113	−17.0				
103		8.1		12.5	−6.7

[a] Band maximum at 258 nm.

A similar reduction of the 240-nm band intensity occurs if the Schiff bases are cooled in the nonpolar solvent: from 13 700 at room temperature the extinction coefficient of **2** in isopentane decreases to 5900 at 123 K.

CD Spectra. With the UV spectra already indicative of geometrical equilibria, it is not surprising that the CD spectra reflect the conformational flexibility of these chiral systems even more. It will prove useful to differentiate between Schiff bases derived from alkylamines (compounds **2**–**5**) and those from hydroxy amines (**6**–**9**).

Temperature dependent CD spectra of **2** in both isopentane and methanol/ethanol are shown in Figures 2 and 3. These spectra are typical for the alkylamine Schiff bases. In both solvents a CD band appears at low temperatures with maximum at 267 (isopentane) or 263 nm (methanol/ethanol). The sign of the band

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Table V. Regression Analyses of Rotational Strength Data of Table IV

	$\Delta G^{\circ a}$	$R_A{}^b$	$R_B{}^b$	r^c
2	0.48	−24	45	0.998
4	0.53	10	−24	0.998
5[d]				
7	0.53	16	−39	0.999
9	0.59	−9	22	0.999

[a] In kcal/mol. [b] In 10^{-40} cgs. [c] Correlation coefficient of regression analysis. [d] No regression possible because of too few data points.

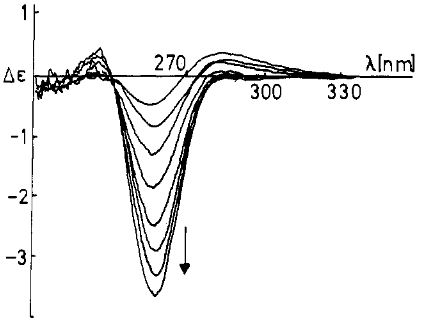

Figure 4. Temperature-dependent CD spectra of **9** in methanol/ethanol. Curves correspond to temperatures of 283, 253, 223, 193, 163, 143, 123, and 103 K.

correlates with the absolute configuration of the asymmetric carbon atom, being negative for *S* (**2**) and positive for *R* (**3**, **4**, and **5**).

The development of the band in the two solvents follows different patterns. In methanol/ethanol, the increase of ϵ is steady over the whole temperature range studied. In contrast, the band in isopentane develops slowly down to about 210 K, with the rate increasing significantly only as the temperature is lowered further.

Rotational strengths obtained from integration of the (digitized) spectra are summarized in Table IV. **3** and **8** are enantiomers of **2** and **7**, respectively, with mirror-image CD spectra. Those data are not included in the table.

The data of Table IV may be rationalized by assuming a temperature-dependent equilibrium between two chiral components.[17] When $1/(1 + \exp(-\Delta G^\circ/RT))$ is plotted against the observed rotatory strength at different temperatures, an excellent correlation is obtained for **2**, with $\Delta G^\circ = 0.48$ kcal/mol and rotatory strengths of -24×10^{-40} and $+45 \times 10^{-40}$ cgs, respectively. The same free enthalpy difference obtains from an analysis of the isopentane data of **2**, but only if the data above 213 K are omitted. The results of the regression analysis of **2** and the other compounds are summarized in Table V.

The CD spectra of the hydroxy amine Schiff bases **6**–**9** in methanol/ethanol are very similar to the ones discussed so far; as an example, the spectra of **9** are shown in Figure 4. There appears, in addition to the strong band with maximum at 258 nm, a weak band of opposite sign at longer wavelengths, which, however, disappears at lower temperatures. The rotatory strengths obtained from the CD spectra of **7** and **9** are included in Table IV, as are the results of the regression analysis in Table V. We note that for these compounds the rotatory strength of the more stable component is positive if the asymmetric carbon is *S* (**6** and **7**) and negative if the chiral center is *R* (**8** and **9**), which is opposite to the results found for the alkylamine Schiff bases.

In nonpolar solvents the CD spectra become more complicated, indicating the influence of additional equilibria. As an example, the spectrum of **6** in isopentane is shown in Figure 5. Down to 213 K, a negative band with maximum at 269 nm develops. As the temperature is lowered further, this band decreases at the cost of a second band that develops at 259 nm and with opposite sign. This low-temperature band agrees in position and sign with the band observed in ethanol. At 133 K, this band completely dominates the spectrum. The other compounds in this group (**7**, **8**, and **9**) behave completely analogously.

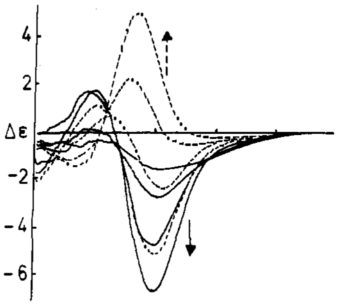

Figure 5. Temperature-dependent CD spectra of **6** in isopentane. Temperatures correspond to (solid curves) 283, 253, 233, and 213 K and (broken curves) 193, 173, 153, and 133 K.

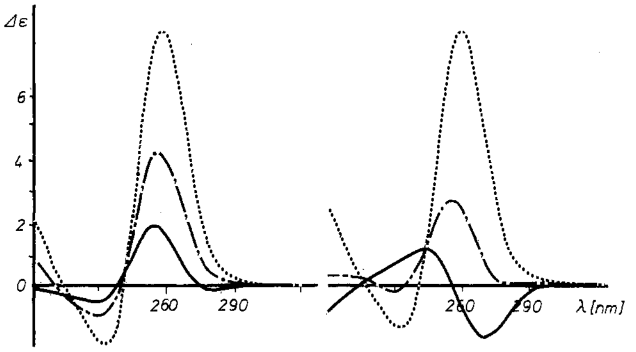

Figure 6. CD spectra of **7** in isopentane at three different temperatures and two concentrations, 1.0×10^{-3} (left) and 8.3×10^{-5} mol/L (right). Temperatures are 193 K (—), 173 K (−··−), and 123 K (···).

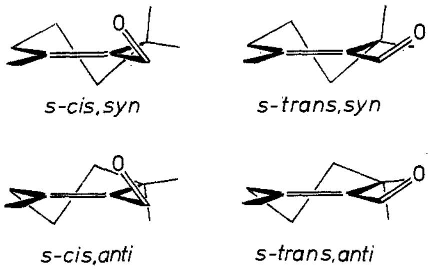

Figure 7. The four diastereomers that may be envisaged for *β*-cyclocitral with *M* helicity.

Only these inverting CD spectra are concentration dependent. The effect of a 12-fold dilution on the spectra of **7** in isopentane at three different temperatures is shown in Figure 6. At 193 K, the diluted solution shows both bands still side by side, while in the concentrated sample the low-temperature band already has taken over the spectrum. At 123 K the spectra are identical again.

Force-Field Calculations. The torsion along the single bond joining the two double bonds is governed both by the cyclohexene ring (assumed to be in the half-chair conformation throughout) and by the amine conformation. In *β*-cyclocitral, only the former is effective, so we will discuss this system first. Depending on the diene conformation (s-cis or s-trans, *P* or *M*) and on the position of the exocyclic double bond relative to the axial of the two methyl groups on C1 (syn or anti), one can differentiate between four pairs of diastereomers. The *M*- configurations are shown schematically in Figure 7.

Both s-trans forms are calculated to be more stable than the s-cis forms by about 1.3 kcal/mol, the reason being the reduced repulsion between the carbonyl oxygen and the C1 methyl groups. The syn/anti discrimination is less severe, amounting to about 0.1 kcal/mol in favor of the anti conformations. The deviation from planarity differs appreciably for the systems, being larger for s-cis (45 and 48° for anti and syn, respectively) than for s-trans (22 and 30°).

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(17) Moscowitz, A.; Wellman, K.; Djerassi, C. *J. Am. Chem. Soc.* **1963**, *85*, 3515.

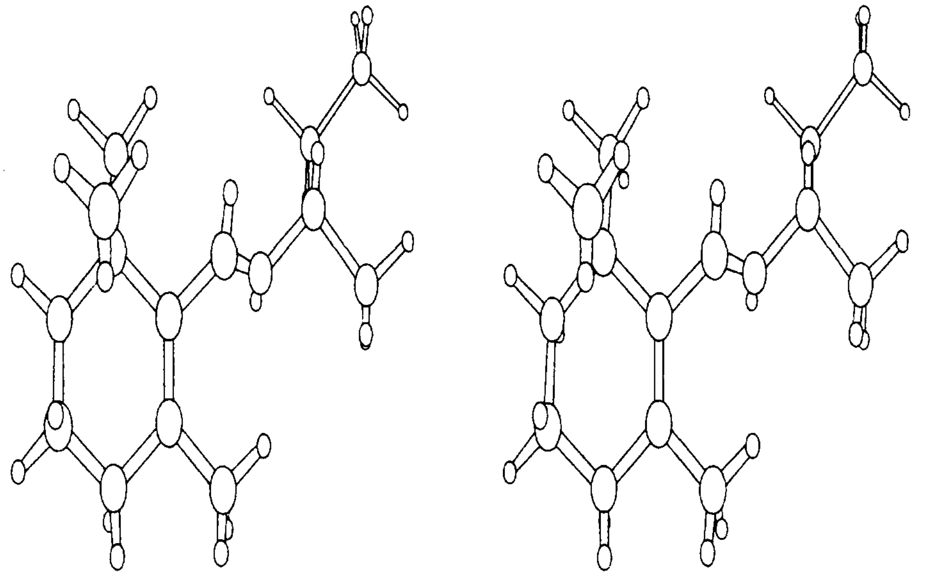


Figure 8. MMP2 stereoplot of the most stable conformation of **2**.

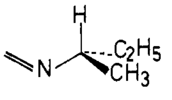
Table VI. MMP2-Calculated Energies and Twist of the Diene System of **2**

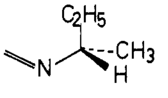
	energy[a]		twist[b]	
	P	*M*	*P*	*M*
s-cis,anti		0.04	54	-50
s-cis,syn	0.29	0.32	55	-49
s-trans,anti	0.35	0.23	164	-169
s-trans,syn	0.02	0.07	151	-150

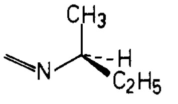
[a] Total energy in kcal/mol relative to s-cis,anti,*P*. [b] In degrees.

Replacing the carbonyl oxygen by the substituted imino group introduces the problem of conformational preference about the C–N single bond; in addition, the chirality of the group renders the *P*/*M* forms of each diastereomer distinguishable. The NMR spectra do not exclude the presence of small (less than 1 %) *Z*-configurated amine in the Schiff bases. The large spectral changes observed in the UV and CD cannot, however, arise from *E*/*Z* isomerization, in line with the high barrier to interconversion of alkylamines[18] and the well-known preference of aldimines for the *E* configuration.[19,20] As a consequence, only the latter was considered in our calculations.

In formaldehyde Schiff base with 2-aminobutane, there are three stable conformations corresponding to a staggered arrangement of the substituents and the nitrogen lone pair:







Of these, the one in which hydrogen eclipses the double bond is found to be more stable than the methyl- and the ethyl-eclipsed conformation by 2.0 and 2.2 kcal/mol, respectively. This preference is no doubt a consequence of the parametrization scheme. It agrees, however, with experimental, mostly spectroscopic, work on substituted alkylamine Schiff bases.[21]

Table VII. CNDO-Calculated Spectral Parameters for the nπ* and ππ* Transition of **2**

	nπ*			ππ*		
	λ[a]	*f*[b]	*R*[c]	Δ[a]	*f*[b]	*R*[c]
s-cis,anti,*P*	278	0.007	-18	225	0.279	4
s-cis,anti,*M*	280	0.007	23	228	0.293	0.3
s-cis,syn,*P*	278	0.008	-6	225	0.267	-12
s-cis,syn,*M*	280	0.007	13	228	0.282	20
s-trans,anti,*P*	303	0.008	9	233	0.580	42
s-trans,anti,*M*	305	0.008	-4	234	0.612	-51
s-trans,syn,*P*	295	0.012	26	228	0.530	-14
s-trans,syn,*M*	295	0.012	-23	228	0.527	12

[a] Position of absorption maximum, in nm. [b] Oscillator strength. [c] Rotatory strengths, in 10^{-40} cgs.

The potential energy function for C–N rotation remains virtually unchanged in going from formaldehyde Schiff base to any of the eight diastereomers of Schiff base **2**, with still a more than 2 kcal/mol preference of the H-eclipsed forms over the other ones. This indicates a rather independent motion about this bond. However, the discrimination of the substituted imine group is sufficient to change the stability order of the diene conformations relative to β-cyclocitral itself. For the H-eclipsed conformations, the numerical results are summarized in Table VI. There is an overall spread in energy of 0.35 kcal/mol, with s-cis,anti, which was rather poor in β-cyclocitral, now being the most stable conformation. A stereoplot of this structure is shown in Figure 8. Very similar results are obtained for Schiff base **6**.

Substitution of the carbonyl group by the imine group destabilizes the s-trans conformations relative to the s-cis forms because of unfavorable interaction of the *gem*-dimethyl group with the alkyl groups of the chiral center. Though of comparable stabilities, the interconversion between s-cis and trans requires considerable energy. The two s-cis minima are separated by a 2 kcal/mole barrier. Barriers of comparable height separate the s-cis from the trans forms, which themselves, however, are easily interconverted over a 0.2 kcal/mol hill.

Chiral discrimination between *P* and *M* helicity is small, ranging from 0.03 for the s-cis,syn conformer to 0.12 kcal/mol for the s-trans,anti conformer.

Electronic Structure Calculations. In these systems with a highly twisted chromophore a clean separation of molecular orbitals into π and σ orbitals is not possible; also, nonbonded electron pairs become highly delocalized, if only for symmetry reasons. Still, inspection of pertinent MO coefficients and of the CI matrix allows a gross classification of the states involved.

Of the many excited states resulting from the CNDO calculation, two stand out because of their low energies and the small number of configurations contributing to them. They are what is best called nπ* and ππ*, and relevant spectroscopic data for

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(18) McCarthy, C. G. *The Chemistry of the C=N Double Bond*; Patai, S., Ed.; Interscience: London, 1969; p 363. Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311. Kalinowski, H. O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.

(19) Karabatsos, G. J.; Lande, S. S. *Tetrahedron* **1968**, 3907. Hine, J.; Yeh, C. Y. *J. Am. Chem. Soc.* **1967**, *89*, 2669.

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(21) Smith, H. E.; Willis, T. C. *Tetrahedron* **1970**, *26*, 107. Casella, L.; Gullotti, M. *J. Am. Chem. Soc.* **1983**, *105*, 803. Buss, V.; Klein, M. *Tetrahedron Lett.* **1984**, *25*, 4487.

both of them in all minimum-energy conformations are gathered in Table VII. Though the energies of the states differ in each conformation, mostly on account of different degrees of twist, the $n\pi^*$ states cluster around 285 nm and the $\pi\pi^*$ states around 230 nm, with the s-trans,anti conformers on account of their rather planar chromophors lying somewhat to the red. The oscillator strengths behave according to expectation, being small with rather irregular changes for the $n\pi^*$ excitations and large for $\pi\pi^*$. In the latter, the f values are about twice as large for the s-trans conformations as compared to s-cis.

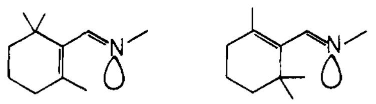
What the oscillator strengths are to the s-cis/trans classification, the signed rotatory strengths of the $n\pi^*$ states are to the helicities of the species involved, with positive values corresponding to M in s-cis and to P in s-trans. The $\pi\pi^*$ state lacks such a correlation, which is surprising since it is generally the (calculated) sign of this state that is used for assignment of helicity in twisted diene systems.[22] On the other hand, the strong influence of chirally disposed substituents on butadiene rotatory strengths[23] and of methyl substitution, especially in allylic position, on twisted butadiene is well-known.[24]

V. Discussion

There can be no doubt that the 240-nm (UV) band and the 265-nm (CD) band correspond, respectively, to the $\pi\pi^*$ and the $n\pi^*$ state of the β-cyclocitral Schiff bases, the relative energies, oscillator strengths, and rotatory strengths all attesting to this fact. The relative order of states agrees with the results of a recent thorough ab initio study on allylidenimine,[25] the unsubstituted chromophore of the Schiff bases. Because of the intensity of the $\pi\pi^*$ absorption, the $n\pi^*$ state is difficult to locate on the basis of UV spectra alone, but it is believed to be the lowest state in conjugated imines.[26] There is a small but consistent blue shift of the CD maximum (267 vs 264 nm) in going from the nonpolar to the polar solvent, in agreement with what would be expected for an $n\pi^*$ absorption.[27] For β-cyclocitral itself, the corresponding wavelengths are 248 ($\pi\pi^*$) and 326 nm ($n\pi^*$), the latter being visible only as a weak shoulder in the UV.[28]

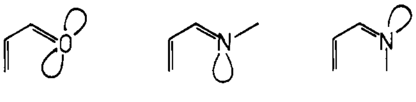
The enormous decrease in intensity of the $\pi\pi^*$ transition upon increasing solvent polarity or lowering the temperature can only result from an s-trans to s-cis isomerization; for a series of sterically crowded enones a reduction in oscillator strengths has been calculated comparable to ours.[29] The low-temperature spectra in isopentane indicate a strong preference of the Schiff bases for the s-cis conformation, in agreement with our calculations, though absolute energy differences are somewhat small. (In passing, we note that for β-cyclocitral the $\pi\pi^*$ absorption becomes more intense as the temperature is lowered,[28] indicating, as do our calculations, that this compound is more stable in the s-trans conformation.)

The preference for the s-cis conformation in methanol already at room temperature could be due to a nonspecific solvent effect or to solvation involving hydrogen bonding with nitrogen as H acceptor. We lean toward the second alternative. Hydroxy amine Schiff bases show the effects of very specific intermolecular hydrogen bonding, if the solvent does not provide for H donors (vide infra). The conformational equilibrium in methanol might thus be determined by the availability of the free electron pair for hydrogen bonding in both geometries:



Inspection of molecular models reveals that the more twisted s-cis conformer is indeed much better suited for this kind of interaction.

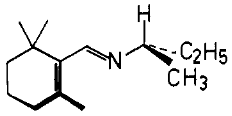
In contrast to the unconjugated azomethine chromophore whose $n\pi^*$ transition acquires rotational strength, albeit of small magnitude,[30] only when placed in a chiral environment, the twisted chromophore of the β-cyclocitral Schiff bases is inherently chiral. As a consequence, the sector rules developed for the C=N bond[31] as well as for salicylaldehyde Schiff bases[32] do not apply here. Qualitative[33] and quantitative MO theory[34] have been advanced to correlate the sign of the $n\pi^*$ CD band with the absolute configuration of nonplanar conjugated enones.[35] Enimines, though isoelectronic with enones, are different because of the second substituent on the heteroatom, which gives rise to E/Z isomers.



The different orientation of the lone pair with respect to the twisted double-bond system will then be a second factor in determining the rotatory strength and might even override the "twist factor". Indeed, in a CNDO/S study on allylidene twisted P-helically from planarity,[36] it was found that the $n\pi^*$ rotatory strength was positive for the E isomer and negative for the Z isomer.

We can rule out, for the systems of this study, any significant contribution from Z isomers. For the s-cis configuration prevailing at low temperature this leaves four different conformations to be considered with a (calculated) energy spread for **2**, e.g., of only 0.32 kcal/mol (Table VI). However, the one calculated to be the most stable (s-cis, anti, P) is also the only one to fit the experimental low-temperature data, which require large negative and small positive rotatory strengths for the $n\pi^*$ and $\pi\pi^*$ transitions, respectively. Calculated (-18×10^{-40} cgs) and experimental (-24×10^{-40} cgs) values for the $n\pi^*$ state agree surprisingly well.

Taking together all experimental and theoretical results, the most probable structure for this molecule is H-eclipsed with respect to the C=N—C fragment and twisted by ca. 54° P-helically from s-cis:



The slight preference of the P- over the M-helical form appears from an analysis of the MMP2 data to be the result of the different steric interaction of the substituents at the chiral center with the C5 methyl group of the cyclohexene ring, the preferred twist juxtaposing this group with the smaller of the two substituents.

The temperature-dependent CD spectra indicate this conformer to be in equilibrium with at least one of opposite chirality. Both the s-cis,anti,M and the s-cis,syn,M conformer of **2** fulfill this requirement, but the large rotatory strength calculated for the $\pi\pi^*$ state of the latter makes this the less likely candidate.

The effect of substitution of the ethyl group by n-propyl (as in **4**) or isopropyl (as in **5**) is only partly what one would expect on the basis of steric arguments. The preferred helicity (M in these cases) still twists the C5 methyl group toward the smaller of the alkyl substituents. However, the expected large increase

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(22) Charney, E. *The Molecular Basis of Optical Activity*; *Interscience*: *New York*, 1979; p 217. Snatzke, G. *Optical Activity and Chiral Discrimination*; Mason, S. F., Ed.; Reidel: Dordrecht, 1979; Part 1, Chapter III, pp 48–53.

(23) Rauk, A.; Peoples, H. A. *J. Comput. Chem.* **1980**, *1*, 240. Burgstahler, A. W.; Barkhurst, R. C. *J. Am. Chem. Soc.* **1970**, *92*, 7601.

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(25) Bonacic-Koutecky, V.; Persico, M. *J. Am. Chem. Soc.* **1983**, *105*, 3388.

(26) Bonnett, R. *The Chemistry of the C=N Double Bond*; Patai, S., Ed.; Interscience: London, 1969; pp 182–202.

(27) Rao, C. N. R. *Ultraviolet and Visible Spectroscopy*; Butterworths: London, 1975; pp 206–210.

(28) Das, P. K.; Becker, R. S. *J. Phys. Chem.* **1978**, *82*, 2081.

(29) Liljefors, T.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 2745.

(30) Bonnett, R. *The Chemistry of the C=N Double Bond*; Patai, S., Ed.; Interscience: London, 1969; pp 202–220.

(31) Ripperger, H.; Schreiber, K.; Snatzke, G. *Tetrahedron* **1965**, *21*, 1027.

(32) Smith, H. E.; Chen, F.-M. *J. Org. Chem.* **1979**, *44*, 2775. Smith, H. E. *Chem. Rev.* **1983**, *83*, 359.

(33) Snatzke, G. *Angew. Chem.* **1979**, *91*, 380; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 363.

(34) Hug, W.; Wagniere, G. *Helv. Chim. Acta* **1971**, *54*, 633.

(35) Snatzke, G. *Tetrahedron* **1965**, *21*, 421, 439.

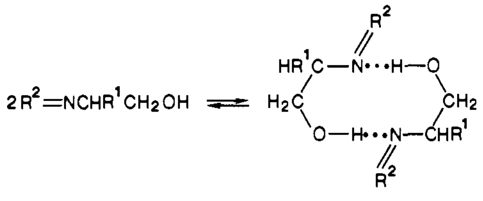
(36) Bystricky, S.; Koos, M.; Repas, M. *Chem. Zvesti* **1981**, *35*, 679.

in discrimination between *M* and *P*, at least for the isopropyl group, is not observed. Energy optimization, which is very time-consuming, has not been performed for these compounds.

The complex behavior of the hydroxy amine Schiff bases may be summarized as follows. In isopentane at ambient temperatures, the preferred helicity of the diene chromophore is *P* for the *S* configuration (**6** and **7**) and *M* for the *R* configuration (**8** and **9**), which sterically leaves the C5 methyl group always pointing away from the hydroxymethyl group, as if this were the larger substituent. According to MMP2 calculations, for **6**, this is indeed the lowest energy conformation. It is not clear, however, why the C5 methyl group prefers, as, e.g., in **9**, even an isopropyl group over the CH_2OH group except if one makes the not unreasonable assumption that interaction with the solvent molecules increases the bulkiness of this very polar group.

The sign inversion at low temperature makes the CD spectra look very similar to the spectra in methanol, not only with respect to the sign of the $n\pi^*$ band but also in its significantly blue-shifted maximum (259 nm in isopentane, 257 nm in methanol/ethanol). Also, the comparable values of the rotatory strengths in both solvents makes the presence of very similar structures highly probable.

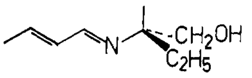
We have shown recently[37] that β-hydroxy amine Schiff bases in nonpolar solvents associate to form what we believe are hydrogen-bonded dimers involving a 10-membered ring structure:



R^1 = alkyl, R^2 = chromophore

The dimerization follows the law of mass action over a wide temperature and concentration range, and thermodynamic parameters for the dimer formation have been obtained.[38] The possible ring conformations can be narrowed down by an analysis of the CD spectra, which show the electronic absorptions exciton-split due to through-space, highly geometry-dependent interaction of the chromophores.

We point out that exciton-splitting is observed for the β-hydroxy amine Schiff base derived from crotonaldehyde[39] while in the analogous Schiff bases with β-cyclocitral it is not. Obviously, in this case the required close contact of the chromophores is prevented because of steric crowding.



That aggregation does occur follows from the concentration dependence of the CD spectra. Moreover, the fact that the low-temperature spectra are independent of concentration (see, e.g., Figure 6) strongly suggests the formation of cyclic dimers probably with the same 10-membered ring structure, albeit in a different conformation with less contact between the β-cyclocitral units.

No aggregate formation is detectable in methanol/ethanol, but hydrogen bonding of the solvent imparts upon the Schiff bases a conformation quite different from the "free-space" conformation in the nonpolar solvent and very similar to the conformation in the dimer. Spectroscopically, this conformation is characterized by sign inversion of the $n\pi^*$ CD band and a blue shift of about 8 nm of its maximum. In terms of structure, this indicates that the enimine with opposite chirality and probably an increased twist angle becomes favored under these conditions.

VI. Summary

Our aim is to relate experimental data and computational results in order to obtain a comprehensive picture about the solution conformations of β-cyclocitral Schiff bases. This attempt is hampered by the multitude of energetically close and easily interconvertible structures as obtained by force-field calculations. It is helped by the fact that UV and CD absorptions are assigned to different excited states and that the geometry dependence of these states is different.

In summary, our results are as follows:

(i) The stable geometry has the two double bonds highly twisted, by about 54°, from s-cis. In hydrogen-bonding solvents, this is the preferred geometry already at room temperature; in nonpolar solvents, it competes against a conformation twisted about 10–20° from s-trans. The torsional potential about the C6–C7 bond is very similar to the one found in retinals.

(ii) The $n\pi^*$ and the $\pi\pi^*$ absorptions are unambiguously assigned, the former dominating the UV spectrum at 240 nm and the latter the CD at 265 nm. The calculated sign of the $n\pi^*$ CD band correlates with the helicity of the twisted enimine chromophore, being plus for *M* and minus for *P*.

(iii) The chiral substituent discriminates between chromophores of opposite chiralities. In nonpolar solvents, *P* is more stable then *M*, if the substituent is *S* configurated. This directs, in the prevailing H-eclipsed conformation, the methyl group on C5 toward the smaller of the two groups at the chiral center.

(iv) Hydrogen bonding, either intermolecularly or with the solvent, stabilizes the oppositely twisted conformation in hydroxy amine Schiff bases.

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(37) Wingen, U.; Simon, L.; Klein, M.; Buss, V. *Angew. Chem.* **1985**, *97*, 788; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 761.

(38) Buss, V.; Simon, L. *J. Chem. Soc., Chem. Commun.* **1986**, *1032*.

(39) Messinger, J. Diplomarbeit, Duisburg, 1986. As is the case with β-cyclocitral Schiff bases, exciton coupling is observed in nonpolar solvents only.