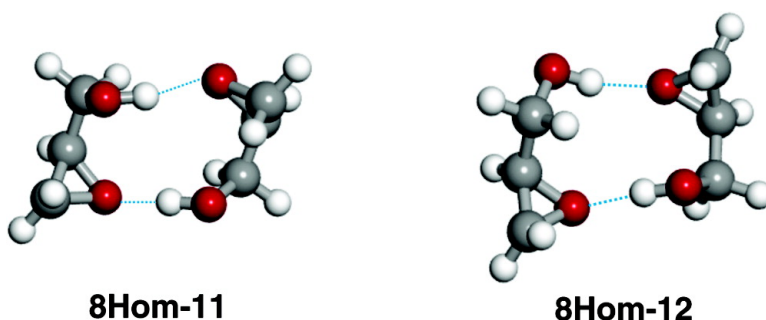


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Molecular Recognition of Chiral Conformers: A Rotational Study of the Dimers of Glycidol

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The role of chirality in favoring the formation and stability of specific aggregates can be investigated through the behavior of relatively simple molecular systems in forming molecular complexes, with the subunits held together through nonbonding interactions. The conformational and dynamical properties of such weakly bound complexes can then guide our understanding of molecular recognition, which characterizes many biological processes.

Various spectroscopic techniques, with different degrees of sensitivity and spectral resolving power, are already established for this purpose. A wealth of results obtained by resonant-two-photon-ionization (R2PI) excitation spectra of the $S_1 \leftarrow S_0$ transition of mass resolved hydrogen bonded molecular complexes have been reported. To observe the electronic transitions of chiral systems, typically their fluorescence spectrum, this technique requires a chromophoric group. Therefore, chiral alcohols with an aromatic ring, such as indan-1-ol, 1-phenyl-1-propanol, 2-naphthyl-1-ethanol, etc., have been investigated.¹ Also gas phase supersonic-jet Fourier transform infrared (FTIR) spectroscopy of the OH-stretching bands was used for this purpose, and clusters of neutral methyl lactate, glycidol, and related aggregates beyond dimers were observed.² Both techniques required complementary theoretical calculations to assign the experimental bands to specific conformers.

Microwave (MW) spectroscopy gives conformational assignment directly from the experimental observations, since it provides the values of the moments of inertia of relatively small molecular systems. A few molecular aggregates have been recently investigated with this technique. The rotational spectrum of a dimeric complex of a chiral molecule has been reported for the first time for butan-2-ol.³ Later on, also oligomers with the chirality induced by the formation of the adducts have been observed by MW spectroscopy, such as the ethanol dimer⁴ or the difluoromethane trimer,⁵ its antipode being obtained by reflection at the CCC plane. Very recently, the rotational spectra of three homochiral and of three heterochiral dimers of propylene oxide have been observed.⁶ In all cases, the direct determination of the moments of inertia of the various species leaves little doubt about their conformations.

Here, we report for the first time the rotational spectra of dimers deriving from the combinations of different conformers of a chiral molecule, glycidol. Its MW spectrum has been reported, and two hydrogen bonded conformers, 1 and 2 (see left column of Figure 1), have been identified.⁷ Conformer 1 is more stable by 3.4 (4) kJ mol⁻¹. As mentioned above, its oligomers have been investigated by Borho and Suhm^{2b} using supersonic-jet FTIR spectroscopy combined with theoretical calculations. We will use here their notations.

The rotational spectra in the 6–18.0 GHz frequency region was measured using a COBRA-type⁸ pulsed supersonic-jet Fourier transform microwave (FT-MW) spectrometer described elsewhere.⁹ A mixture of 0.1% glycidol in He was expanded from ca. 2 bar to $\sim 10^{-5}$ mbar. (*R*)-(+)- (97%) and racemic glycidol (96%) were supplied by Aldrich and used without further purifications.

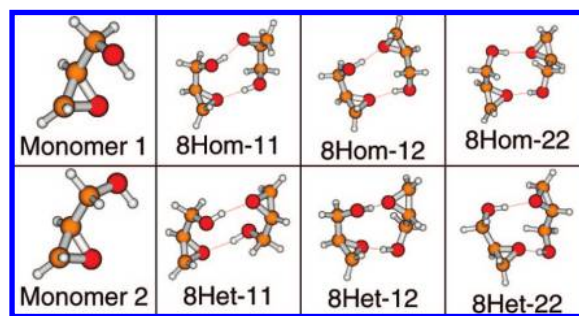


Figure 1. 8Hom and 8Het conformers of glycidol dimer.

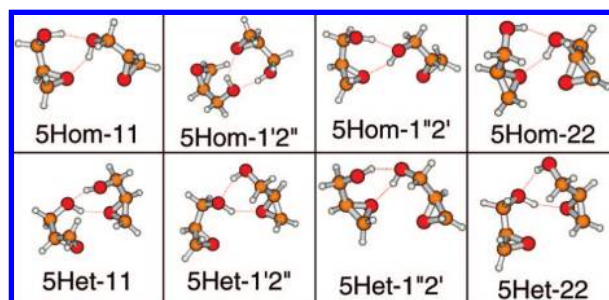


Figure 2. 5Hom and 5Het conformers of glycidol dimer.

In this investigation, we have been interested only in the most stable dimers, the ones stabilized by two, relatively strong, O–H...O hydrogen bonds. A pure chiral species (either *R* or *S*) forms seven hydrogen bonded homodimers (labeled Hom) of this kind. A heterodimer arises from a complex between an *R* and an *S* species.

According to Borho and Suhm^{2b} they can be divided into two groups: one group where the hydrogen bonds form a ring involving eight heavy atoms and another group where this ring involves only five heavy atoms. They will be called 8Hom and 5Hom, respectively. The six (three Hom and three Het) conformers with an eight-heavy-atom frame are shown in Figure 1. There digits 1 and 2 denote the type of monomer conformation (M1 and M2 in the left column of Figure 1).

In Figure 2 we show the eight (four Hom and four Het) conformers with a five-heavy-atom frame.

An estimation of the spectroscopic constants and of the relative energies of the 14 dimers was obtained by quantum chemical calculations at the MP2/6-311++G** level using the Gaussian03 package of programs.¹⁰ In Table 1 we report the results obtained, while a graphical overview of the relative energies and D_c and D_0 binding energies (corrected and uncorrected for basis set superposition error, BSSE) are given as Supporting Information.

We started the search of the spectrum on a homochiral sample, for which only seven dimers can be observed. As suggested by the

Table 1. Ab Initio (MP2/6-311++G**) Rotational Constants, Dipole Moment Components, and BSSE Corrected Electronic Energies Relative to the Most Stable (8Hom-11) Dimer

	A/MHz	B/MHz	C/MHz	μ_a /D	μ_b /D	μ_c /D	E/kJ mol ⁻¹
8Hom-11	2067	805	666	0.0 ^a	0.0 ^a	-2.2	0.0 ^b
8Hom-22	1746	870	692	0.0 ^a	0.0 ^a	0.5	2.2
8Hom-12	1827	833	637	-0.4	-1.7	0.3	1.0
8Het-11	2303	748	648	0.0 ^a	0.0 ^a	0.0 ^a	1.5
8Het-22	1685	882	660	-0.7	0.3	0.1	2.4
8Het-12	1748	852	627	0.2	-1.0	0.8	2.8
5Hom-11	2264	663	574	-0.4	0.3	-0.3	4.0
5Hom-22	1728	837	745	2.5	-2.8	0.8	1.3
5Hom-1'2'	2366	580	512	-1.0	-0.1	1.7	6.1
5Hom-1'2''	1917	759	659	0.4	-0.5	-0.3	5.3
5Het-11	2000	803	751	-0.2	0.2	-0.1	2.0
5Het-22	1738	855	715	2.4	2.4	1.7	5.2
5Het-1'2'	2137	757	642	0.7	-1.0	-0.9	6.2
5Het-1'2''	2046	654	548	-0.7	1.2	-0.9	4.4

^a Zero value by symmetry. ^b Absolute energy: -535.379857 E_h.

Table 2. Experimental Spectroscopic Constants of the Observed Conformers of Glycidol Dimer

	8Hom-11	8Hom-12
A/MHz	2045.2484(5) ^a	1839.4132(5)
B/MHz	800.5695(2)	828.8247(1)
C/MHz	658.4713(4)	636.61874(9)
D _J /kHz	0.135(4)	0.188(1)
D _{JK} /kHz	2.03(2)	1.58(1)
D _K /kHz	-0.15(5)	[0.0] ^b
d ₁ /kHz	-0.027(2)	-0.0586(8)
d ₂ /kHz	-0.0176(3)	-0.0244(5)
σ /kHz	1.5	2.0
N ^c	27	35

^a The error (in parentheses) is expressed in units of the last digit.

^b Not determined in the fit, fixed to zero. ^c Number of transitions in the fit.

relative energies and by the values of the dipole moment components, we searched for μ_c and μ_b type transitions of species 8Hom-11 and 8Hom-12, respectively. We observed the two spectra, both of them very weak, and could measure 27 μ_c and 35 μ_b transitions, respectively. J_{\max} and K_{\max} were 8 and 11, and 2 and 3, respectively. They were fitted with a Watson's type Hamiltonian¹¹ (S-reduction I' representation), obtaining the spectroscopic constants reported in Table 2. A comparison with the theoretical values of the rotational constants leaves no doubt about the conformational assignments. No detectable lines assignable to the remaining Hom species were observed in the spectrum.

We then analyzed the rotational spectrum of the racemic mixture. We observed, as expected, a considerable reduction (ca. 50%) of the intensities of the rotational transitions of the 8Hom-11 and 8Hom-12 species. We could not detect any new measurable line. This is not surprising, because the expected most abundant hetero species, 8Het-11, does have a center of symmetry and then its dipole moment is zero. Also the two next stable Hetero species, 8Het-12 and 5Het-11, are difficult to observe, due to their very low values of the dipole moment components.

However, based on its relative energy and μ_a and μ_b values, one would expect to observe the spectrum of the 5Hom-22 conformer, at least in the pure chiral species. But one has to take into account that the abundance ratio of two dimers in the supersonic expansion is not directly related to their relative energies: besides thermody-

namics, there is a kinetic-statistic factor in establishing the relative concentration. Since the ratio of the monomeric species M1 and M2 molecules is ~4:1 at the temperature in the pre-expansion, we have to consider that a glycidol molecule does have the quadruple of probability to encounter a one- rather than a two-partner molecule at the nozzle position where the supersonic expansion starts.

By comparing the intensities of several pairs of nearby transitions, we obtained the relative abundance of the two adducts, according to the following equation:¹²

$$N_{8\text{Hom-12}}/N_{8\text{Hom-11}} = (I_{8\text{Hom-12}}\mu_{c,8\text{Hom-11}}\gamma_{8\text{Hom-11}}\nu_{8\text{Hom-11}}) / (I_{8\text{Hom-11}}\mu_{b,8\text{Hom-12}}\gamma_{8\text{Hom-12}}\nu_{8\text{Hom-12}})\exp(-\Delta E_{\text{rot}}/kT_{\text{rot}})$$

where I , γ , μ_a , and ν are the peak height, line strength, dipole moment component, and frequency, respectively, of the considered transition. ΔE_{rot} is the energy difference between the two lower levels of the pair transitions, and T_{rot} (~1 K) is the rotational temperature in the jet.

The result, $R_{8\text{Hom-12}/8\text{Hom-11}} (= N_{8\text{Hom-12}}/N_{8\text{Hom-11}}) = 1.3 \pm 0.4$, is close to the value expected under conditions of thermodynamic equilibrium. However the lack of the spectrum of the 5Hom-22 species, which has an energy very close to the one of 8Hom-12 and high values of two dipole moment components (see Table 1), indicates that the kinetic-statistic factor mentioned above plays an important role.

FTMW spectroscopy is a tool which gives precise information in chiral recognition, enabling for the first time the detection of molecular adducts of different conformers of a chiral molecule.

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Supporting Information Available: Complete ref 10, Tables of transition frequencies and of D_e and D_0 binding energies, and Graphical overview of the relative energies of the various dimers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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