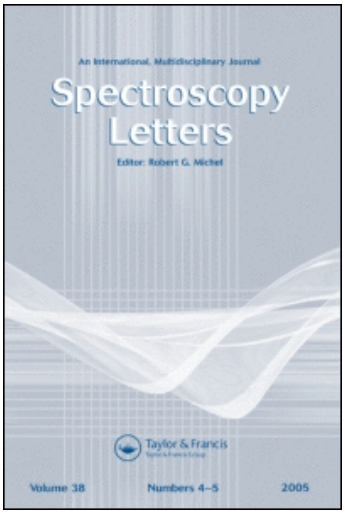


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Conformational Equilibrium of Tetralenediols-2,3 by PMR Method

A. Postawka[a]; L. Prajer-janczewska[a]; K. Rudolf[a]
[a] Institute of Chemistry, Wroclaw University, Poland

To cite this Article Postawka, A. , Prajer-janczewska, L. and Rudolf, K.(1979) 'The Conformational Equilibrium of Tetralenediols-2,3 by PMR Method', Spectroscopy Letters, 12: 3, 207 — 217
To link to this Article: DOI: 10.1080/00387017908069147
URL: http://dx.doi.org/10.1080/00387017908069147

SPECTROSCOPY LETTERS, 12(3), 207-217 (1979)

THE CONFORMATIONAL EQUILIBRIUM OF TETRALENEDIOLS-2,3 BY PMR METHOD

A.Postawka, L.Prajer-Janczewska,K.Rudolf

Institute of Chemistry,Wrocław University,Poland

The conformational equilibrium of trans-2,3-dihydroxy-tetraline was studied by the ^{1}H-NMR method,on the basis of the methin protons signal width measurements.The metylene and methin protons of the alicyclic tetralene-diol ring represent the AB CC' A'B' system /Fig.1,2/. The spectrum data are time averages of the values corresponding to the diaxial /a,a/ and diequatorial /e,e/ conformations and depend upon their ratio. The methin protons /C C'/ signal width /J, the distance measured between outer strong peaks, or at the 1/4 signal height/ equals $J_{AC} + J_{BC} + J_{A'C} + J_{B'C}$ [1].Itis also represented by the equation $J = nJaa + /1-n/Jee$, where Jaa and Jee are the signal widths in the diaxial and diequatorial forms res-

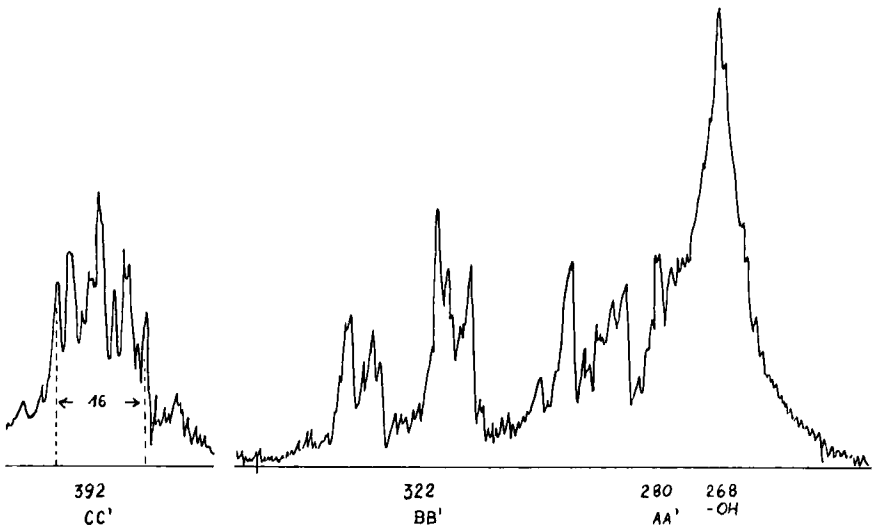


Fig. 1a: TRANS - DIOL Solvent CD_2Cl_2, Sweep width 270

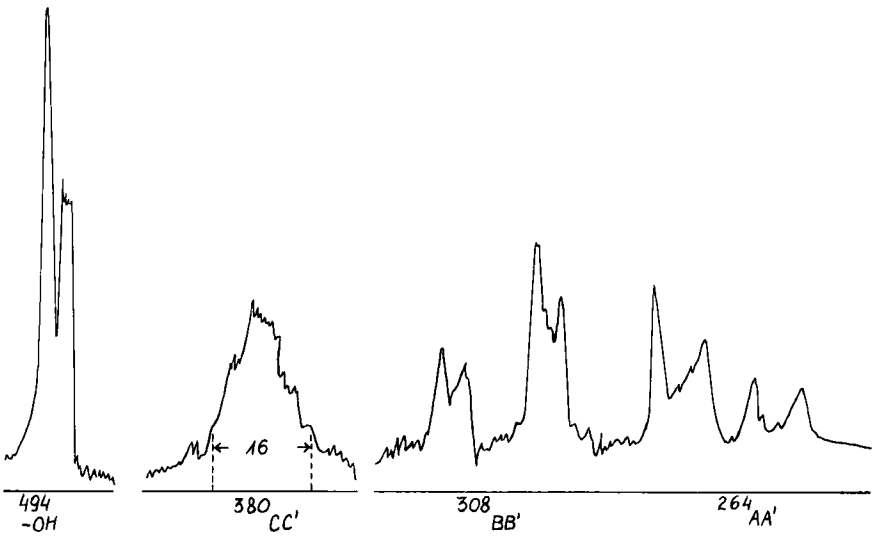


Fig. 1b: TRANS - DIOL Solvent DMSO, Sweep width 270

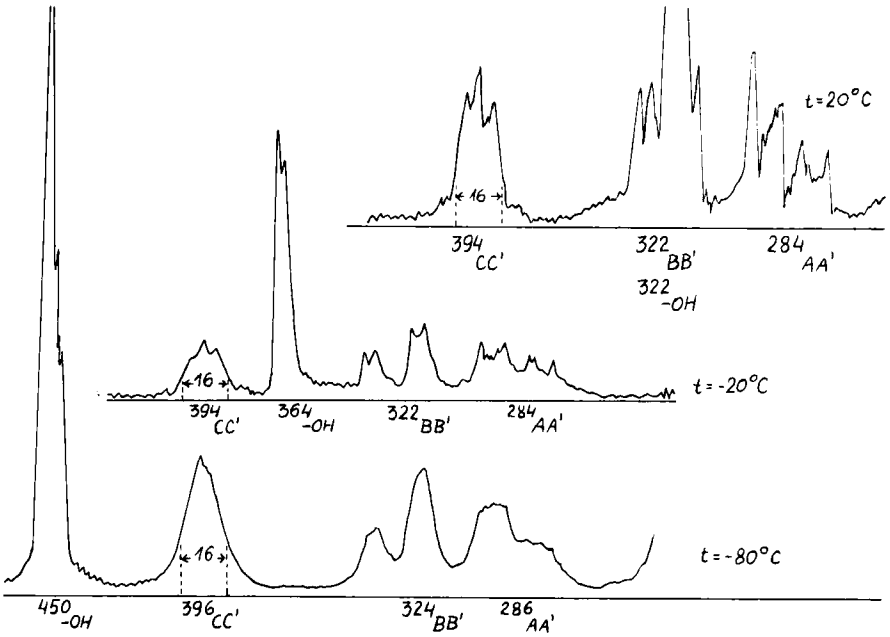


Fig. 2: TRANS - DIOL Solvent $CO/CD_3/_2$, Sweep width 540

pectively, and n is the molar fraction of the diaxial form.

We intended to base our calculations on the J value of cis isomer, which constitutes the 50% conformational equilibrium, assuming rather the same J value for the analogical equilibrium of trans-diol:

$$J_{/cis/} = \frac{Jaa + Jee}{2} \qquad /1/$$

as well as on the proportion $\frac{Jaa}{Jee} \approx \frac{1}{3}$ /2/

The equation /1/ would arise from an approximation, obtained with the aid of the more significant coupling constants J_{AC} and J_{BC} /neglecting the long-range couplings $J_{A',C}$ and $J_{B',C}$ and the electronegativity influences/. These couplings were taken from the Karplus diagram for the corresponding dihedral angles of the alicyclic tetralin ring. The structure of this ring is analogical to that of cyclohexene, for which the half--chair form has been calculated as the most stable one[2]. The endocyclic dihedral/torsional/ angles of tetralin: $\Psi_{1,2} = \Psi_{3,4} = 45^\circ$ and $\Psi_{2,3} = 60^\circ$ [1]. According to the assumption of the pseudotrigonal projection symmetry of the fragment X-CH_2-CH_2-Y and the relationship:

$$\varphi_{aa} = 120 + \Psi, \quad \varphi_{ee} = 120 - \Psi, \quad \varphi_{ae} = \Psi \text{ [3]},$$

/Ψ = X-C-C-Y torsional angle, φ = H-C-C-H dihedral angle/, for the fragments:

$$\overset{/A,B/}{\underset{/1/}{}} \overset{/C/}{\underset{/2/}{}} \qquad \overset{/C'/}{\underset{/3/}{}} \overset{/B'A'/}{\underset{/4/}{}}$$

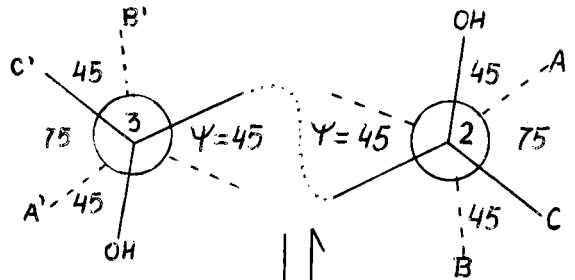
$$\gtrless C - CH_2 - CH(OH) - \quad , \quad -(HO)CH - CH_2 - C \lessgtr$$

the following values of the dihedral /φ/ angles can be written: $\varphi_{aa} = 120 + 45 = 165^\circ$, $\varphi_{ee} = 120 - 45 = 75^\circ$, $\varphi_{ae} = 45^\circ$; for trans- and cis-diol this is illustrated

by the structures:

trans

a,a



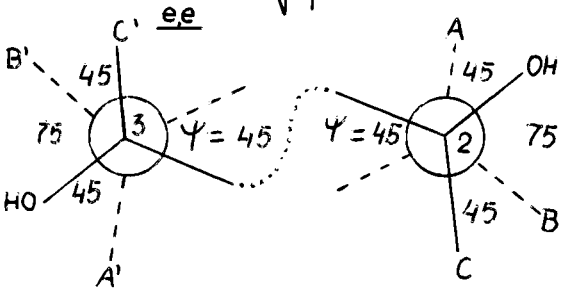
the coupling constants from the Karplus diagram

$J_{A'C'} = J_{AC} = 0,5\ (\varphi ee)$

$J_{B'C'} = J_{BC} = 4\ (\varphi ae)$

$J\alpha\alpha = 4,5$

e,e



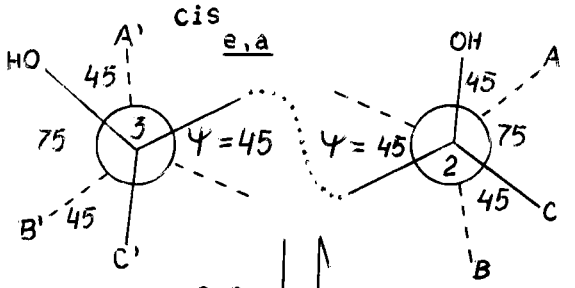
$J_{A'C'} = J_{AC} = 9,5\ (\varphi\alpha\alpha)$

$J_{B'C'} = J_{BC} = 4\ (\varphi ae)$

$Jee = 13,5$

cis

e,a

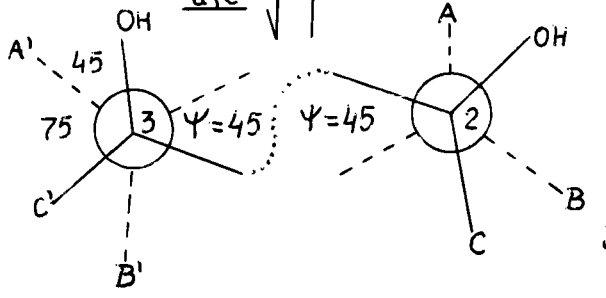


$J_{A'C'} = 9,5\ (\varphi\alpha\alpha)$

$J_{B'C'} = J_{BC} = 4\ (\varphi ae)$

$J_{AC} = 0,5\ (\varphi ee)$

a,e



$J_{A'C'} = 0,5\ (\varphi ee)$

$J_{B'C'} = J_{BC} = 4\ (\varphi ae)$

$J_{AC} = 9,5\ (\varphi\alpha\alpha)$

$J = \frac{9,5 + 0,5 + 4 + 4}{2} = 9$

Therefore for the 50% equilibrium of trans diol:

$$J = \frac{Jaa + Jee}{2} = 9 = J_{/cis/}$$

The proportion /2/ would arise also from the approximate J values: $\frac{Jaa}{Jee} = \frac{4,5}{13,5} = \frac{1}{3}$, as well as from the literature data[1] for the similar compounds /e.g. for the 2,3-dichlorotetralin, Jaa = 7, Jee= 20,1 /.

Unfortunatelly the J value of the cis compound proved not to contain the long range couplings, which was rather strange,as well as the fact,that the protons A and B appeared to be equivalent /triplet for the methin and doublet for the methylene protons /. Probably it is accidental,because like as in trans diol, none of the methylene protons occur here in the same magnetic environment at any time. Considering cis diol as useless for our calculations we have examined one of the diastereomeric derivatives of trans diol , trans monoester/Fig 3/, obtained by oppening of the 2,3-tetralene epoxide ring by the chiral/+/-camphoro-sulfonic acid. This compound with the big substituent instead of the one hydroxyl proton was expected to exist mainly in the diequatorial form, which in lower temperatures should be assumed as the 100% one. Indeed the J value of this compound /23 -24 Hz/ even exceeded the expected one[1]

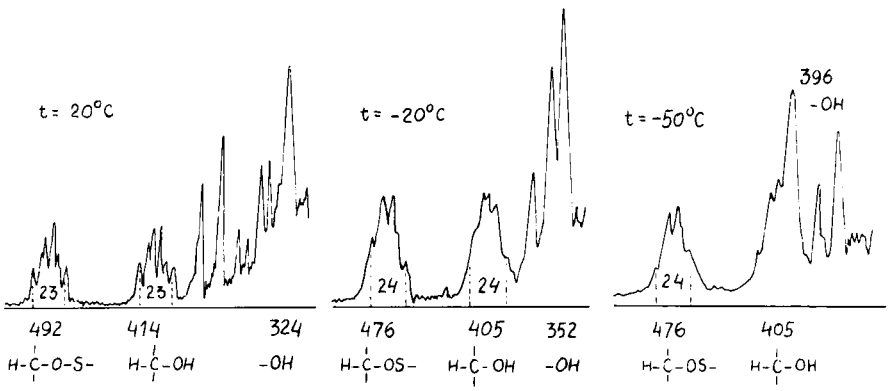


Fig. 3: MONO-ESTER OF TRANS-DIOL Solvent $CDCl_3$, Sweep width 1080

and did not change at -20 and -50°C. The substitution of the hydroxyl proton by the sulfonyl rest was found not to influence the methin proton signal width /the same signal width for the protons C and C'/.

According to /2/ and assuming Jee = 24 Hz, we can obtain Jaa = 8 and J = 16. In the case of polar solvents like DMSO or $CO/CD_3/_2$ we have to take into account the broadening of methin protons signal width by the additional coupling with hydroxyl protons, and to use the proper J value. The difference between the J-values of cis /Fig.4/ and trans /Fig.1,2/ diol /in 50% equilibrium/ would equal 4 Hz, which could be ascribed to the long range couplings in such conformational relation of the trans compound. The larger J values of cis diol,

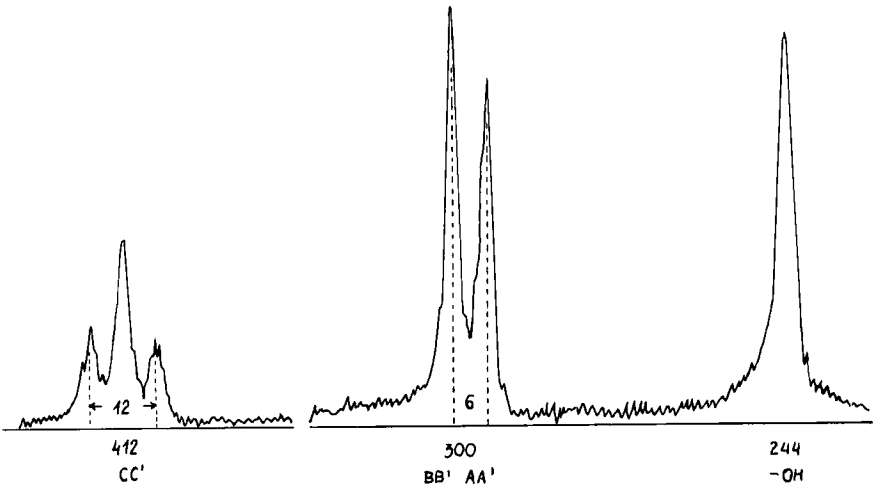


Fig. 4a: CIS - DIOL Solvent CD_2Cl_2, Sweep width 270

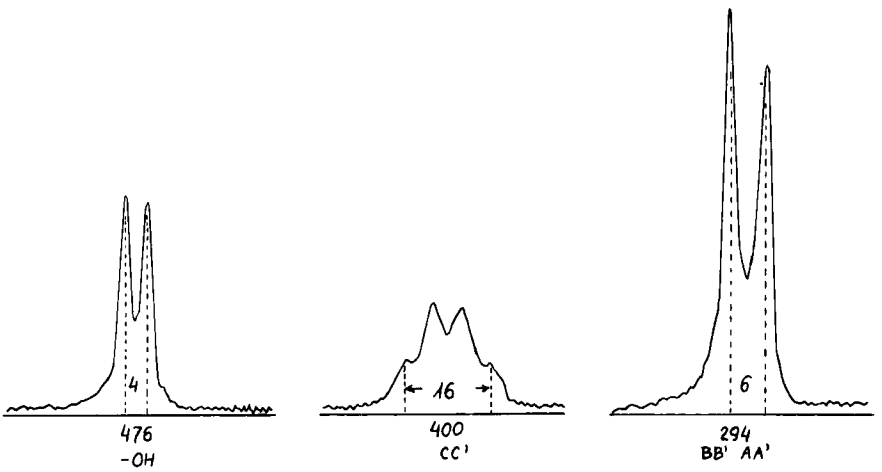
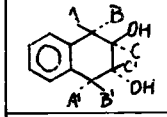
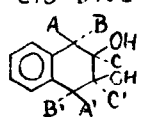


Fig. 4b: CIS - DIOL Solvent DMSO, Sweep width 270

then that calculated from the dihedral angles, may result from the electronegativity of the hydroxyl protons.

As it is evident from the Table 1, in the conformational equilibrium of trans diol the diequatorial form does not predominate, what is in agreement with the literature data for the dihalogenoderivatives[1]. However, the percentage of aa-form decreases more in DMSO. This fact could be explained by larger steric hindrances in the equatorial positions for the two big substituents, formed by the DMSO molecules strongly associated to the hydroxyl protons. As a result of such intermolecular bondings we observe the mutual splitting of the methin and hydroxyl protons, as well as the downfield shift of the last one. Similar situation is in $CO/CD_3/_2$, however, the hydrogen bonds with the solvent become stronger here only at the lower temperatures /Table 1/. The hydroxyl proton signals are not so clearly splited, they are rather broadened. The lack of an excess of diequatorial form for trans diol in the other solvents would indicate rather weak intramolecular hydrogen bondings, which is also confirmed by the high-field signal positions of the hydroxyl protons. The same fact can be noticed for cis diol, supported also by the clearly averaged coupling constants testifying for the fast conformational interconversion.

TABLE 1

COMPOUND	SOLVENT	T °C	CHEMICAL SHIFTS OF THE PROTONS (Hz) AROMATIC	METHIN (CC') >CH(OH)	METHIN (CC') >CH(OS)	METHYLENE (BB')	METHYLENE (AA')	OH	$J_{C(OH)}$ = $J_{C'(OH)}$ (Hz)	J-VALUES (Hz)	MOLAR FRACTION (n) OF aa FORM
TRANS-DIOL 	C_6D_6	20	694	358 (m)	–	294	260	196		15,5	0,53
"	CD_2Cl_2	20	726	392 (m)	–	322	280	268		16	0,50
"	DMSO	20	722	380 (m)	–	308	264	494 (d)	3	16-3=13	0,69
"	$CO(CD_3)_2$	20	726	394 (m)	–	322	284	322	broadening	16-2=14	0,62
"	"	-20		394 (m)	–	322	284	364	2	16-2=14	0,62
"	"	-80		396 (m)	–	324	286	450	2	16-2=14	0,62
MONO-ESTER OF TRANS-DIOL	$CDCl_3$	20	712	414 (m)	492 (m)					23	0,06
"	"	-20	694	405 (m)	476 (m)					24	0,00
"	"	-50	702	405 (m)	476 (m)					24	0,00
CIS-DIOL 	CD_2Cl_2	20	727	412 (t)	–	300 (d)		244		12	
"	DMSO	20	724	400 (q)	–	294 (d)		476 (d)		16-4=12*	

* for cis-diol $J_{AC} = J_{BC} = 6$ Hz

EXPERIMENTAL

The PMR spectra are obtained on JEOL JNM-PS-100 Spectrometer.TMS was used as the internal standard.The J values were measured using a Scale expansion of 7,5 Hz/cm.

ACKNOWLEDGMENT

The autors are thankful to Polish Academy of Sciences for financial support.

REFERENCES

1. M.R.Buys,C.H.Leeuwestein, E.Havinga, Bull.Trav.Chim., 88, 1233 /1969/.
2. C.W.Beckett,N.N.Freeman,K.S.Piter, J.Am.Chem.Soc., 70, 4227 /1948/.
3. J.B.Lambert,Acc.Chem.Res., 4, 87 /1971/.

Received 1-23-79
Accepted 2-06-79