CARBON-13 SPIN-LATTICE RELAXATION IN DIASTEREOISOMERS

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Abstract Carbon-13 spin-lattice relaxation times were measured in diastereoisomeric (*cis-trans, E-Z, eq.-ax., endo-exo, meso-racemic*) pairs of alicyclic and aliphatic compounds. In all cases carbon atoms in the more crowded isomers have longer relaxation times as compared with those in the less crowded isomer. The differences in relaxation times are large (8 to 60%) and can be used for the assignment of spectral lines and for the identification of individual diastereoisomers.

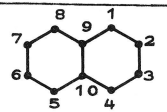
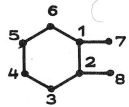
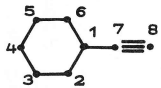
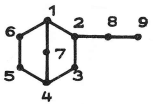
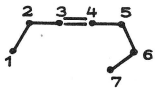
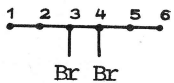
Introduction Different mutual orientations of atoms in various types of diastereoisomeric organic compounds result in a variety of molecular shapes and steric interactions in these isomers, leading to different effective correlation times and the corresponding relaxation times. In a general case it is rather difficult to relate ^{13}C relaxation data to specific intramolecular steric interactions, mainly because of the multitude of conformational, anisotropy of rotation and other effects that must be taken into account.[1] Surprisingly, no systematic comparative study of ^{13}C relaxation times in isomers has up to now been carried out.

Experimental The ^{13}C T_1 values were measured over a wide temperature range on a Bruker WH-90 spectrometer at 22.63 MHz using the $(T-\pi-t-\pi/2)_n$ pulse sequence, see Table. All T_1 values were rechecked by long signal accumulations at t values chosen to maximize the differences in the intensities of signals from the isomers being compared. In order to guarantee the best possible conditions for T_1 comparison and to exclude the influence of H_1 and H_o inhomogeneity as well as that of possible impurities and macroscopic viscosity, 1:3 to 1:1 mixtures of pure isomers were used as neat liquids. Prelimi-

nary experiments with decalin showed that dissolved oxygen causes only an insignificant increase in the overall ^{13}C relaxation rate [$T_1(O_2) \approx 150$ to 240 sec] and the samples were therefore not degassed. With the exception of methyl groups, ^{13}C relaxation was dominated by the dipole-dipole interaction in all cases.

Discussion The overall relaxation pattern parallels earlier findings with shorter relaxation times found for carbons located at or near the main axis of rotation.[2] Such differences are largest (twofold for C_4) between the equatorial and axial conformers of cyclohexylacetylene at -80°C. Molecular tumbling is very anisotropic for the equatorial conformer and nearly isotropic for the axial one. In dimethylcyclohexanes the more crowded 1,2-*cis*; 1,3-*trans* and 1,4-*cis* dimethyl derivatives have higher densities and consequently smaller effective molecular volumes and shorter correlation times τ_c than the other diastereoisomer, and are characterized by longer T_1 values on all carbons. The same is true for norbornane derivatives and in decalins, where at low temperatures (-30°C) the chair-chair interconversion in *cis*-decalin is slow on the NMR time scale and also at high temperatures, where this conversion is rapid, but still very slow in comparison with τ_c. In aliphatic compounds the *z*-isomers have, as expected, the longer relaxation times and this difference exists even between the racemic and meso-forms. In 3,4-dibromohexane[3] the meso-isomer has higher density ($d_4^{25} = 1.594$, $n_D^{25} = 1.5049$) than the racemic form ($d_4^{25} = 1.589$, $n_D^{25} = 1.5031$) and again, the relaxation times are longer in the former. Steric interactions, which lead to significant diamagnetic shifts of the methylene carbons in the α-position to the double bond in *z*-n-alkanes, lead to no measurable relaxation effects or unusual T_1 ratios between the isomers. ^{13}C relaxation effects are best explained by anisotropic molecular tumbling or segmental rotation. Tumbling aniso-

TABLE CARBON-13 NUCLEAR RELAXATION TIMES IN DIASTEREOISOMERS

Compound	Formula	Diastereo isomer	Total chem. shift $\Sigma\delta_C$	Content %	T °C	^{13}C spin-lattice relaxation times, multiplied by the number of protons directly attached NT_1								
						C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	$C_{9,10}$
Decalin		trans	334.8	40	-30	1.6	1.2	1.2	1.6	1.6	1.2	1.2	1.6	1.0
		cis	290.4	60		2.0	1.4	1.4	2.0	2.0	1.4	1.4	2.0	1.6
		trans		40	54	11.8	11.4	11.4	11.8	11.8	11.4	11.4	11.8	9.7
		cis		60		13.6	12.4	12.4	13.6	13.6	12.4	12.4	13.6	11.7
		trans		40	54*	13.0	12.0	12.0	13.0	13.0	12.0	12.0	13.0	10.6
		cis		60		14.2	13.0	13.0	14.2	14.2	13.0	13.0	14.2	12.7
1,2-Dimethyl cyclohexane		trans	246.1	25	30	14.0	14.0	16.2	15.2	15.2	16.2	21.9	21.9	
		cis	211.2	75		15.9	15.9	20.0	19.0	19.0	20.0	24.0	24.0	
Cyclohexyl-acetylene		eq.	331.6	82	-80	0.8	0.8	0.8	0.4	0.8	0.8	-	0.6	
		ax.	318.5	18		1.0	1.0	1.0	0.8	1.0	1.0	-	1.2	
2-Ethyl-bicyclo-[2.2.1]-heptane		exo	300.1	35	30	9.3	8.5	11.4	8.2	10.2	-	9.8	13.2	10.6
		endo	290.8	65		10.7	10.7	13.4	9.6	-	12.6	10.8	13.4	11.6
Heptene-3		E-	373.5	35	30	30.0	28.0	16.0	16.0	28.0	26.0	36.0		
		Z-	362.8	65		48.0	36.0	22.0	21.0	36.0	32.0	43.8		
		E-		100	30	31.2	27.0	15.5	15.2	29.2	25.6	34.2		
		Z-		100		45.9	36.6	21.4	20.5	34.4	30.4	42.9		
3,4-Dibromo-hexane		meso	203.8	40	30	9.0	5.2	4.0	4.0	5.2	9.0			
		racemic	204.5	60		7.8	4.6	3.7	3.7	4.6	7.8			

* degassed.

tropy is largerly a molecular property, as evidenced by the very closely similar relaxation data for pure isomers and the equimolar mixture. Faster ^{13}C relaxation in the less crowded diastereoisomer with a larger sum of all ^{13}C chemical shifts $\Sigma\delta_C$ is a useful extension of the Auwer's rule and has considerable analytical significance.

References

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SPIN-LATTICE RELAXATIO

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Abstract The ^{29}Si and
nuclear Overhauser enh
siloxanes (M_4Q, M_3T an
predominates over spin
T groups and ^{13}C) and
laxation times are con
tral core and rapid ro

Introduction Small ne
ral abundance make the
^{29}Si nuclei in organic
data are available abou
situation is further c
intramolecular rotation
attached to silicon. In
thus gain importance an
molecular microdynamic
skeleton-forming nuclei
with measurements in a
ble to gain considerabl
organosiloxanes.

Experimental The ^{29}Si
and nuclear Overhauser
tures between 213 and 4
M_3T and M_4T_2, where M=M
using 13 mm OD spherica
than ±1°C. A universal
in the Fourier and Hada