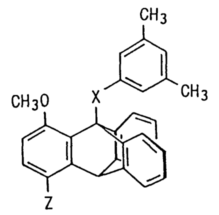
NOTES Bull. Chem. Soc. Jpn., 62, 4058—4060 (1989)

Detailed Dynamic NMR Study of a Molecular Gear, 1-Methoxy-9-(3,5-dimethylbenzyl)triptycene

Gaku YAMAMOTO
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113
(Received June 29, 1989)

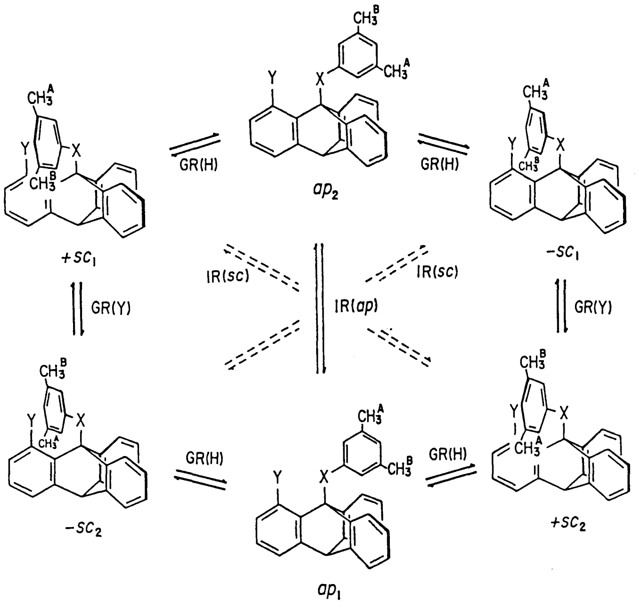
Synopsis. Stereodynamics of the title compound was studied by dynamic NMR spectroscopy. The "isolated" rotation of the aryl group was found to have a lower barrier than the correlated gear rotation.

In 1979, we reported a dynamic NMR study of 9-(3,5-dimethylbenzyl)triptycene derivatives,[1)] which behave as molecular gears composed of a two-toothed wheel and a three-toothed one.[2)] We pointed out the presence of two fundamental processes, gear rotation (GR), in which the correlated disrotation of the aryl group (Ar) and the triptycene moiety (Tp) occurs, and "isolated" rotation (IR) of the Ar group without rotation of the Tp moiety. At that time, the NMR spectra were measured on a 60-MHz CW spectrometer and the analysis was made by an approximate method, in which only the rate constant at the coalescence temperature was obtained. Thus some of the data were somewhat unreliable and the conclusion drawn therefrom was simplistic. We therefore decided to reinvestigate this topic, by obtaining variable temperature NMR spectra of a typical derivative, 1-methoxy-9-(3,5-dimethylbenzyl)triptycene (**1**), at 270 MHz in the FT mode and analyzing the data by total line-shape analysis.



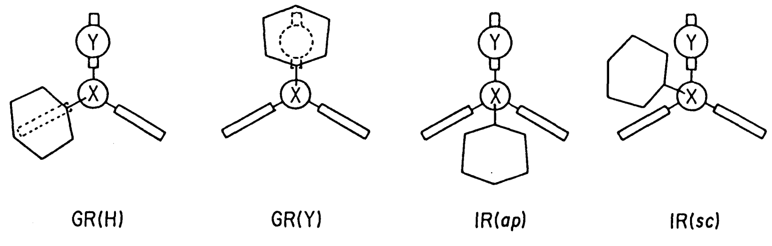
1 X=CH$_2$, Z=H
2 X=O, Z=OCH$_3$

The possible dynamic processes exhibited by the molecules of **1** are shown in Scheme 1. Three sites are available about the Tp-CH$_2$ bond, i.e. *ap*, +*sc*, and −*sc*, and thus six conformers should be considered if the two *m*-methyl groups are differentiated. Processes shown at the periphery in the Scheme constitute a gear rotational circuit, which comprises two kinds of primary steps; GR(H) in which the aryl group passes over a peri-hydrogen, and GR(Y) in which the aryl group passes over the peri-substituent Y. In each step the edge of the aryl rotor interchanges; each *m*-methyl group points inside and outside alternatively. Two other motions should be taken into account; isolated rotations of the aryl group at the *ap* and ±*sc* sites, designated as IR(*ap*) and IR(*sc*), respectively. Isolated rotation of the Tp moiety may be neglected because the plausible transition state of this process, in which the aryl group and one of the benzene ring of the triptycene skeleton becomes coplanar, is highly unlikely. Transition states of these processes are schematically shown as Newman projections along the Tp-X bond axis in Scheme 2. Therefore, four independent rate constants are necessary to describe the whole processes exhibited by the molecule at a given temperature.



Scheme 1.

At −98.1 °C, the lowest attainable temperature, internal rotation of both the Tp-CH$_2$ and Ar-CH$_2$ bonds is frozen and two isomers, *ap* and ±*sc*, are separately observed in the ^{1}H NMR spectrum in CD$_2$Cl$_2$ (Fig. 1). The major isomer present in 70% at



Scheme 2.

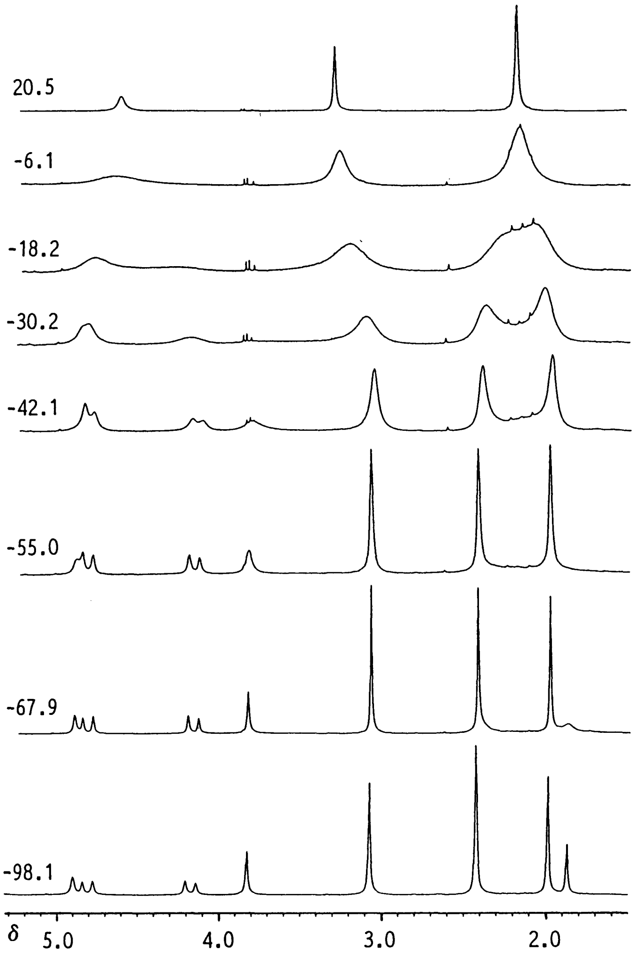


Fig. 1. ^{1}H NMR spectra of **1** in CD_2Cl_2 at several temperatures (°C). Impurity peaks are seen at δ 2.1—2.3, ca. 2.6, and 3.8—3.9 regions.

this temperature is assigned as ±*sc*; the methylene protons give an AB-quartet signal (δ 4.17 and 4.80, J=17.4 Hz) and the methoxyl proton signal appears at a high field of δ 3.07 because of the ring current effect of the benzylic aryl group. The minor isomer assigned as *ap* gives a singlet at δ 4.90 for the methylene protons and a singlet for the methoxyl protons at a normal position of δ 3.82. The *m*-methyl protons of the benzylic aryl group appear as a pair of singlets for each isomer, although the low-field peaks are overlapped (*ap*: δ 1.87 and 2.42; ±*sc*: δ 1.98 and 2.42). The two higher-field singlets are reasonably assigned to the methyl groups pointing inside (CH_3^B in ap_1 and $\pm sc_1$ and CH_3^A in ap_2 and $\pm sc_2$).

The signals broaden and coalesce as the temperature rises, and a broad singlet is observed for each of the methyl, methoxyl and methylene protons at room temperature.

Table 1. Kinetic Parameters Obtained from DNMR

Compd	Process	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta G^{\ddagger}_{200}$
		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}
1	GR(H)[a]	10.6±0.1	−4.1±0.5	11.5±0.1
	GR(Y)			>12.7
	IR(*ap*)	9.6±0.2	−3.1±0.8	10.2±0.1
	IR(*sc*)			>12.7
2[b]	GR(H)			<7.7[c]
	GR(Y)	11.8±0.2	−0.9±0.7	12.0±0.2
	IR(*ap*)			>12.0
	IR(*sc*)			≫12.0

a) The kinetic parameters refer to the *ap*→*sc* process. b) Ref. 2c. c) Reinvestigated. No splitting down to −100 °C at 500 MHz.

The dynamic NMR behavior of the 1-methoxyl proton signal, in which two unequally intense singlets at low temperature coalesce into a single peak, corresponds to the $ap\rightleftarrows\pm sc$ interconversion which occurs by the GR(H) process and is described by a single rate constant, $k(ap\rightarrow\pm sc)$, which we refer to as $k_{\mathrm{GR(H)}}$. The rate constant for the reverse process, $k(\pm sc\rightarrow ap)$, is related to $k_{\mathrm{GR(H)}}$ by the equilibrium constant K. Line-shape analysis of the spectra at nine temperatures between −6 and −55 °C as a one-spin two-site system using the DNMR5[3] and/or DNMR3K[4] program affords the best-fit values of $k_{\mathrm{GR(H)}}$ and the kinetic parameters for the GR(H) process (Table 1).

The methylene proton signal is composed of a singlet due to *ap* and an AB-quartet due to ±*sc*. The line-shape is controlled by two independent rate constants. The one is $k_{\mathrm{GR(H)}}$ and the other describes the direct interconversion between +*sc* and −*sc* corresponding to the GR(Y) process. Careful examinations revealed that the observed spectra are excellently reproduced with $k_{\mathrm{GR(Y)}}$ of zero and $k_{\mathrm{GR(H)}}$ obtained from the analysis of the methoxyl signal, suggesting that $k_{\mathrm{GR(Y)}}$ is very small relative to $k_{\mathrm{GR(H)}}$. Actually, incorporation of $k_{\mathrm{GR(Y)}}$ larger than one twentieth of $k_{\mathrm{GR(H)}}$ distinctly deviates the calculated spectrum from the observed one. Therefore, the GR(Y) process has a free energy barrier of at least 1.3 kcal mol^{-1} (1 cal= 4.184 J) higher than that of GR(H).

The dynamic NMR behavior of the *m*-methyl proton signal is somewhat complex. Four singlets (apparently three because of the overlap) at low temperature coalesce into a single peak. In the DNMR5 program, the case is treated as a one-spin four-site system. Four sites represent *ap*-in, *ap*-out, *sc*-in, and *sc*-out. The *ap*-in⇄*sc*-out and *ap*-out⇄*sc*-in motions correspond to GR(H) and *ap*-in⇄*ap*-out to IR(*ap*). The *sc*-in⇄*sc*-out conversion may occur either by GR(Y) or by IR(*sc*) and the dynamic NMR analysis can not predict which is actually occurring. *ap*-in⇄*sc*-in and *ap*-out⇄*sc*-out are assumed to be negligible. Detailed analysis of the spectra shows that only two non-zero rate constants corresponding to GR(H) and IR(*ap*) are required to reproduce the observed spectra. Line-shape analysis of the spectra at seven temperatures between −42 and −80 °C using the extrapolated values of $k_{\mathrm{GR(H)}}$ obtained as described above affords the best-fit values of $k_{\mathrm{IR}(ap)}$ and the kinetic parameters for the IR(*ap*) process (Table 1).

The *sc*-in⇄*sc*-out process and hence both of GR(Y) and IR(*sc*) have again free energy barriers of at least 1.3 kcal mol^{-1} higher than that of GR(H).

It is interesting to compare the present results with those previously reported for the corresponding ether analog, 1,4-dimethoxy-9-(3,5-dimethylphenoxy)triptycene (**2**).[2c)] We assume that the 4-methoxyl group in **2** has no significant effect on the dynamic processes discussed here.

In the ^{1}H NMR spectra of **2**, the 1-methoxyl signal appears as a sharp singlet in the whole temperature range studied, and the methyl protons give a singlet at room temperature but two equally intense singlets below −18 °C.[2c)] This indicates that the GR(H) barrier is very low (<7.7 kcal mol^{-1}) and the observed dynamic process should be explained by either GR(Y), IR(*ap*), or IR(*sc*) as the rate-determining step. Molecular mechanics studies by MM2 revealed that GR(Y) has the lowest barrier and therefore the observed process was assigned to GR(Y) as shown in Table 1.[2c)]

The results given in Table 1 show that **1** has higher barriers for the GR processes than **2** but lower barriers for the IR processes. This is understood in terms of the differences in valencies (tetravalent in **1** and divalent in **2**) and in bond lengths (1.49—1.55 Å for C–C and 1.36—1.42 Å for C–O), as discussed in detail in the previous papers.[2b,c)] The valency effect would predominate over the bond length effect at the GR transition states, where the eclipsing interactions occur at three sites in **1** and at only one site in **2**. Meanwhile the bond length effect would predominate at the IR transition states, where the ortho hydrogens of the Ar group are closer to the Tp skeleton in **2** than in **1**.

In conclusion, in compound **1** the gear rotation is not the minimum energy process while in the ether analog **2** the meshed gearing is the most favorable process.

Experimental

Synthesis of **1** has been described.[1)]

Variable temperature ^{1}H NMR spectra were obtained on a JEOL GX-270 spectrometer operating at 270.17 MHz in the FT mode using a ca. 4% (w/v) solution of **1** in CD_2Cl_2. Temperatures were calibrated using a methanol sample and are reliable to ±0.5 °C.

Line-shape analysis was performed either on a Hitac M-680H computer system at the Computer Center of the University of Tokyo using the DNMR5 program[3)] or on a NEC PC-9801F personal computer equipped with a Graphtec MIPLOT II plotter using the DNMR3K program.[4)] Temperature dependence of the rotamer populations, chemical shift differences, and T_2 values was properly taken into account.

References

1) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1979**, 1251; *Bull. Chem. Soc. Jpn.*, **54**, 473 (1981).

2) a) G. Yamamoto, *J. Mol. Struct.*, **126**, 413 (1985) and references cited therein. b) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1984**, 97; *Bull. Chem. Soc. Jpn.*, **58**, 1953 (1985). c) *idem, ibid.*, **59**, 3597 (1986).

3) D. S. Stephenson and G. Binsch, *QCPE*, No. 365.

4) A modified version of the DNMR3 program[5)] converted for use on personal computers by Dr. H. Kihara of Hyogo University of Teacher Education.

5) D. A. Kleier and G. Binsch, *QCPE*, No. 165.