^{1}H-NMR Study of the Aromatic-ring Motion in 3,12-Dithia[4.4]metaparacyclophanes

Kazuhiko Tsuchiya, Tetsuo Takemura, and Nobuo Mori*
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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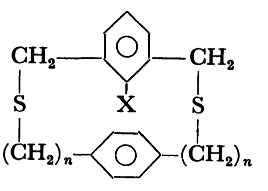
Synopsis. In 10-substituted 3,12-dithia[4.4]metaparacyclophanes, the free energy barrier to the rotation of the para-bridged ring increases with the substituent in the order: H<F<CH_3O<Cl, whereas for the flipping of the meta-bridged ring, the order of CH_3O and Cl is reversed. This is discussed in terms of the steric-size anisotropy of the CH_3O group.

There have been several ^{1}H-NMR and stereochemical studies of the aromatic-ring motion in [2.2]- and 2,11-dithia[3.3]metaparacyclophanes. In [2.2]metaparacyclophane itself, the meta-ring can flip[1] even with a sizable energy barrier to flipping,[1-4] but the para-ring can not rotate because of the severe nonbonded interaction between the para-ring and the 8-hydrogen atom.[1,3,4] In the dithia[3.3]phanes,[4,5] where there is a much weaker interaction between the para-ring and a substituent at the 9-position, it becomes easier for both rings to move, the facility being dependent on the steric size of the 9-substituent.[5]

In the present work, we have investigated the relative motility of the two benzene rings in 3,12-dithia[4.4]- and 4,13-dithia[5.5]metaparacyclophanes, **1—5**, by means of ^{1}H-NMR spectroscopy.



Compound	*n*	X
1	2	H
2	2	F
3	2	Cl
4	2	CH_3O
5	3	CH_3O

In **1—5**, the rotation of the para-ring and the flipping of the meta-ring were followed separately, as was done in the dithia[3.3]phanes,[5] by variable-temperature measurements of the 100-MHz spectra of the para-ring protons and of the meta-bridged benzylic methylene protons.

In **1**, the para-ring and the 4,11-methylene protons showed sharp, temperature-independent singlets at δ 6.83 and 3.45 respectively down to −51 °C, indicating a rapid rotation of the para-ring and a rapid flipping of the meta-ring in the temperature range examined. The bridging ethylene protons also showed a temperature-independent AA′BB′ multiplet down to −51 °C.

In **2**, the para-ring and the methylene protons showed sharp singlets at δ 6.70 and 3.44 respectively at room temperature; each of them became broader as the temperature dropped down to −51 °C. The ethylene protons showed an AA′BB′ multiplet at room temperature; this multiplet approached an ABCD system with the drop in the temperature.

In **3**, the para-ring protons showed two narrow AA′XX′ multiplets centered at δ 6.44 and 6.87 at room temperature; they coalesced to a broad singlet at 88 °C and became a sharp singlet at 120 °C. On the other hand, at room temperature the 4,11-methylene protons showed an AB quartet (δ 3.35, 3.69; J=15 Hz) which coalesced at 133 °C. The ethylene protons showed a very wide, unsymmetrical, finely split ABCD multiplet at low temperature; this multiplet approached an AA′BB′ multiplet with the rise in the temperature.

The low-temperature spectrum of **4** was very similar to that of **3**. The two multiplets due to the para-ring protons (δ 6.48, 6.80) coalesced at 54 °C, whereas the AB quartet due to the two-methylene protons (δ 3.29, 3.64; J=15 Hz) was temperature-independent up to 162 °C. The ethylene protons gave an ABCD multiplet at low temperatures; this multiplet approached an AA′BB′ system with the rise in the temperature.

In **5**, the para-ring protons showed a temperature-independent sharp singlet down to −51 °C, whereas the 5,12-methylene protons gave, at −40 °C, an AB quartet (δ 3.38, 3.84; J=15 Hz) which coalesced at 15 °C.

The table gives the free-energy barriers to ring motion ($\Delta G^{\neq}$), estimated using the chemical-shift difference at a low temperature ($\Delta\nu$) and the coalescence temperature (T_c).[6] It can be noticed that, in **1—4**, the free-energy barrier to rotation of the para-ring increases with X in the order: H<F<CH_3O<Cl, whereas for the flipping of the meta-ring the order of CH_3O and Cl

Table 1. ^{1}H-NMR data for compounds **1—5**

Compound	X	Solvent	Protons concerned	$\Delta\nu$/Hz	T_c/°C	$\Delta G^{\neq}$/kcal mol^{-1} [b]
1	H	$CDCl_3$	*p*-ArH	—	≪−51	—[c]
			m-$ArCH_2$	—	≪−51	—[c]
2	F	$CDCl_3$	*p*-ArH	—	<−51	—[c]
			m-$ArCH_2$	—	<−51	—[c]
3	Cl	DMSO-d_6	*p*-ArH	43.0[a]	88	18
			m-$ArCH_2$	33.8[a]	133	21
4	CH_3O	DMSO-d_6	*p*-ArH	32.0	54	16
			m-$ArCH_2$	34.9	≫162	>22
5	CH_3O	$CDCl_3$	*p*-ArH	—	≪−51	—
			m-$ArCH_2$	46.3	15	14

a) Values in $CDCl_3$. b) 1 cal=4.184 J. c) Since the spectrum of **2** was temperature-dependent but that of **1** was temperature-independent, $\Delta G^{\neq}$ for **2** can be expected to be larger than that for **1**.

is reversed.[7] This may be explained in terms of the anisotropy of the steric size of the methoxyl group. If the para-ring rotation is influenced dominantly by the nonbonded interaction of X with the para-ring, the free-energy barrier should correlate with the net size of the C-X moiety, which can be approximately estimated as the sum of the bond length of C_{sp^2}–X and the steric size (or the van der Waals radius) of X. This is the case only, however, when X is a single atom: the order of the net size is 2.2 for H<2.7 for F<3.5 Å for Cl. For CH_3O, the net size is estimated to be *ca.* 4.0 Å in the direction along the C–OCH_3 bond axis, but this is too large. Molecular models suggest that, in **4**, the CH_3 moiety of the CH_3O group is not a severe obstacle to the rotating of the para-ring when it is not very much distorted out of the plane of the attached meta-ring. Neglecting the steric size of the CH_3 moiety, the size estimation leads to a net size of *ca.* 2.8 Å (the sum of the bond length of C_{sp^2}–O and the van der Waals radius of O), a value between those for F and Cl. Thus, this or a somewhat larger size seems rather reasonable.

On the other hand, the meta-ring flipping may be influenced not only by the above X$\cdots$para-ring interaction, but also by the nonbonded interaction of X with the bridging chains. This interaction should be dependent on the van der Waals radius of X, if X is a single atom. Of importance for CH_3O is the net size in the direction along the O–CH_3 bond axis, when the CH_3 moiety is substantially coplanar with the attached meta-ring. The order of the size of X estimated in this way is 1.2 for H<1.35 for F<1.8 for Cl<3.4 Å for CH_3O, in agreement with the order of $\Delta G^{\ne}$.

The lower $\Delta G^{\ne}$ values for **5** give further evidence for the dependence of the ring motions on the length of the bridging chains or on the nonbonded interaction between X and the para-ring.

Experimental

Samples. **1** was prepared by the literature method:[8] Mp 81.0 °C. **2**—**5** are unknown and were similarly prepared using the corresponding 2-substituted *m*-xylenes.

2: Mp 113.3—113.8 °C; Found: C, 67.78; H, 6.02; S, 19.51%; M^+, 318. Calcd for $C_{18}H_{19}S_2F$: C, 67.89; H, 6.01; S, 20.13%; M^+, 318.

3: Mp 132.1—132.4 °C; Found: C, 64.70; H, 5.73; S 19.05%; M^+, 334. Calcd for $C_{18}H_{19}S_2Cl$: C, 64.55; H, 5.72; S, 19.15%; M^+, 334.

4: Mp 93.4—94.2 °C; Found: C, 69.00; H, 6.79; S, 19.08%; M^+, 330. Calcd for $C_{19}H_{22}S_2O$: C, 69.05; H, 6.71; S, 19.40%; M^+, 330.

5: Mp 80.2—81.3 °C; Found: C, 70.75; H, 7.35; S, 17.90%; M^+, 358. Calcd for $C_{21}H_{26}S_2O$: C, 70.34, H, 7.31; S, 17.89%; M^+, 358.

^{1}H-NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer (100 MHz) for solutions of *ca.* 10 w/v% in dimethyl-d_6 sulfoxide or chloroform-*d*; the measurement temperature was that in the probe. Mass spectra were recorded on a HITACHI M-80 spectrometer.

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