

2,11-DITHIATRIS[3.3.2]PARACYCLOPHANES. EFFECTS OF INTERNAL ROTATION OF BENZENE RINGS IN MACROCYCLOPHANES ON NMR SPECTRA

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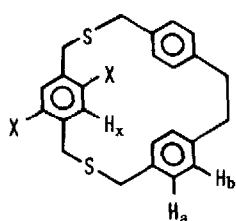
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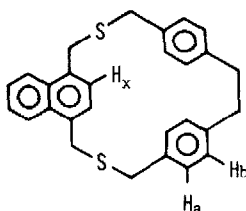
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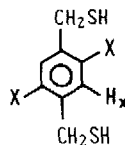
In order to improve yield and to overcome difficulties in preparations of cyclophanes,¹ several routes *via* thiacyclophane derivatives have often been explored as the useful preparations, especially for syntheses of [2.2]-type compounds.² The authors have attempted to prepare 2,11-dithiatris[3.3.2]paracyclophanes as new macrocyclic compounds and also as starting materials to the syntheses of larger systems such as tris[2.2.2]paraxylylene.³ Now the authors wish to report the preparations of these dithiacyclophanes (Ia-e and II) and some interesting characteristics in NMR chemical shifts of aromatic protons connected



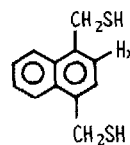
Ia X = H
 Ib X = F
 Ic X = Cl
 Id X = Me
 Ie X = OMe



II



IIIa X = H
 IIIb X = F
 IIIc X = Cl
 IIId X = Me
 IIIe X = OMe



IV

with internal rotation of benzene rings.

Ia-e and II were prepared by coupling reactions between 4,4'-bis(chloromethyl)bibenzyl and sodium salts of the corresponding dithiols (IIIa-e and IV) in benzene-ethanol under the high dilution conditions: Ia (Y = 55 %), mp 162.0-162.5°; Ib, (18 %), mp 131.1-131.9°; Ic, (37 %), mp 113.0-113.5°; Id, (23 %), mp 143.2-143.5°; Ie, (15 %), mp 163.0-163.5°; II, (46 %), mp 192.0-193.0°. All of the compounds thus obtained gave satisfactory elemental analyses and mass spectra.

Table 1. Chemical Shifts of H_x and $H_{a,b}$ Protons.^a

Compd	H_x	$H_{a,b}$	Compd	H_x
Ia	6.30(s)	7.02(s)	IIIa	7.25(s)
Ib	6.67(t) ^b	6.87(AA'BB')	IIIb	7.03(t) ^c
Ic	7.31(s)	6.82(AA'BB')	IIIc	7.37(s)
Id	6.87(s)	6.71(AA'BB')	IIId	7.02(s)
Ie	6.54(s)	6.83(AA'BB')	IIIe	6.79(s)
II	6.12(s)	6.97(s)	IV	7.36(s)

a. In $CDCl_3$ at 31.5°, δ (ppm) from internal TMS.

b. $J(H-F) = 8.3$ Hz. c. $J(H-F) = 8.1$ Hz.

The chemical shifts of the aromatic protons (H_x and $H_{a,b}$) recorded in $CDCl_3$ at 31.5° on a 100 MHz instrument are summarized in Table 1. The most striking result is that the chemical shifts of the H_x protons in Ia and II are observed in very high field as for macrocyclophanes,⁴ while those of the H_a and H_b protons in Ia and II locate in normal aromatic region. Since the rotation of the A ring and the B rings in Ia is possible based on the molecular model (CPK), the observed chemical shift represents an average value at various rotational conformations. Thus, the upfield shift of the H_x protons in Ia, by 0.95 ppm compared with the H_x in IIIa, is attributed to the *statistical* transannular shielding effect of the B rings as shown in Fig. 1, where the A ring

prefers a "lateral"⁵ conformation and the B rings "face"⁵ conformations. This interpretation is supported with the larger upfield shift of the H_x in II than Ia, because the benzo substituent of the A ring in II is too large to rotate and therefore the H_x protons are forced to locate close to the B rings.

The high field shifts of the H_x signals in Ib-e are small but still appreciable. The magnitude of the shifts compared with the parent dithiols are in the decreasing order Ib, Ie, Id and Ic, which is just in accord with the increasing steric effect⁶ of the substituents. That is, although the complete "lateral" conformation is not allowed for Ib-e due to steric repulsion between the substituents and the B rings,

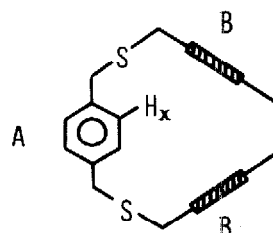


Fig. 1

the A ring can incline more largely from the "face" conformation with decreasing of the steric effect of the substituents.

The temperature dependence of the chemical shifts of the H_x protons measured in CS_2 at low temperatures and in $DMSO-d_6$ at high temperatures are shown in Fig. 2. The high field shifts with lowering of the temperature (from 150° to -105° for Ia,c-e and II, and to -100° for Ib) amount to 0.95, 0.13, 0.05, 0.10, 0.39 and 1.20 ppm⁷ for Ia-e and II, respectively. Remarkable large shifts are seen again for Ia and II, which indicate that at low temperatures the internal rotation of the B rings becomes slow on the NMR time scale and the population

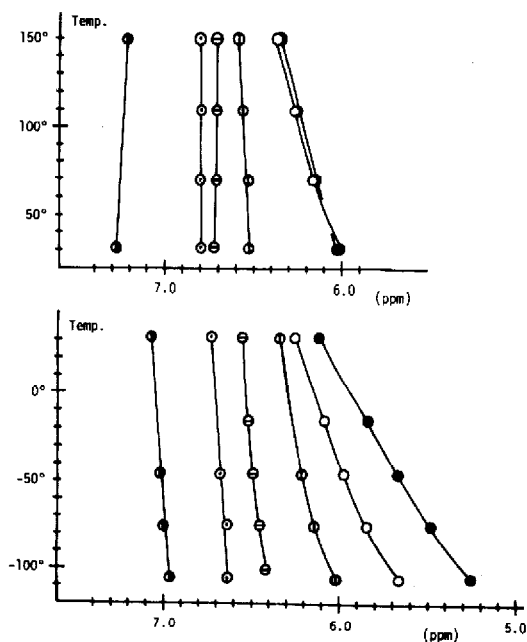


Fig. 2 Temperature dependence of the chemical shifts of the H_x protons: \circ , Ia; \ominus , Ib; \bullet , Ic; \odot , Id; \oplus , Ie; \bullet , II. The upper; in $DMSO-d_6$, δ from internal hexamethyldisiloxane. The lower; in CS_2 , δ from internal TMS.

of the "face" conformation of the B rings increases, whereas the internal rotation of the A ring does not become slow on the NMR time scale.⁸

Another interesting result is the relatively large upfield shift of the H_x protons in Ie, which may be explained with the following consideration that the A ring in Ie prefers to take the inclined conformation at low temperatures in order to avoid repulsion between π electron clouds of the "face" benzene rings and the A ring, where π electron density of the A ring increases by substitution of the two methoxyl groups.

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7. These values are obtained from simple additions of the shifts in the high and the low temperatures, *i.e.*, for Ia, 0.95 (ppm) = 0.35 (150°-31.5°) + 0.65 (31.5°-(-105°)).
8. The temperature dependence of the chemical shifts of the H_a and H_b protons is very small; -0.18 ppm for Ia and -0.30 ppm for II, and the splitting of the H_x protons in Ia is at most 2 Hz at -105° (100 MHz).