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NMR STUDY OF HIGH PRESSURE EFFECTS ON MOLECULAR CONFORMATIONS OF 2,11-DITHIA[3.3.1]PARACYCLOPHANE AND 2,11-DITHIA[3.3.2]PARACYCLOPHANE

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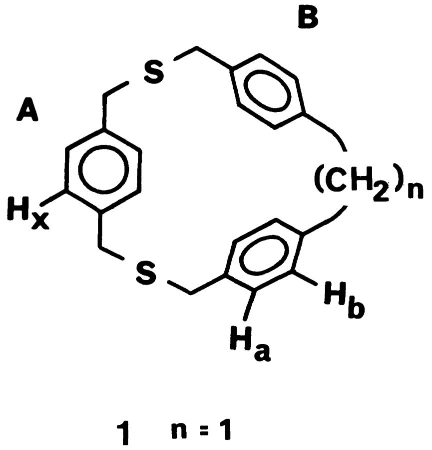
A high-pressure high-resolution NMR study for 2,11-dithia[3.3.n]-paracyclophanes (n=1,2) revealed that the H_x protons of ring A shift notably to high field, whereas the $H_{a,b}$ protons of ring B move to low field. Reduction of the partial volumes under high pressure, being effected by changes in the dihedral angles, is responsible for the chemical shift changes.

Under high pressures of a few kilobars, molecules are expected to change their dihedral angles to reduce their partial volumes. Although such contraction has been detected by various spectroscopic techniques, such as high-pressure infrared spectroscopy,$^{1)}$ there still have been reported only few reports. Recently techniques of measuring high-resolution NMR spectra under high pressure have



1 n = 1
2 n = 2

Table 1. Proton chemical shifts for 2,11-dithia[3.3.1]paracyclophane, 1, and 2,11-dithia[3.3.2]paracyclophane, 2, under pressure.[a)]

		H_x	$H_{a,b}$	$-CH_2SCH_2-$	$-CH_2-$
	$\delta(1)^{b)}$	453.5	575.1	231.3, 214.1	240.8
1	$\delta(1500)$	445.8	579.5	233.7, 214.3	244.7
	$\delta\Delta^{c)}$	-7.7	4.4	2.4, 0.2	3.9
	$\delta(1)$	487.1	560.0	229.1, 218.2	165.1
2	$\delta(1500)$	478.0	564.7	230.8, 218.3	168.9
	$\delta\Delta$	-9.1	4.7	1.7, 0.1	3.8

a) Chemical shifts were measured in $CDCl_3$ at 100 MHz and 35.0°C ± 0.3°C. Concentrations of solutions were less than 1 mol%. Values are given in Hz. b) $\delta(p)$ denotes the chemical shift from internal cyclohexane under a pressure of p bar. c) $\delta\Delta = \delta(1500) - \delta(1)$.

been reported,[2,3)] and have aroused an increasing interest as a new tool in high-pressure studies. This report presents notable pressure effects on the proton chemical shifts and conformational properties of 2,11-dithia[3.3.1]paracyclophane, 1,[4)] and 2,11-dithia[3.3.2]paracyclophane, 2,[5)] observed by use of a simplified version[3)] of high-pressure high-resolution NMR techniques.

The proton NMR spectra were obtained under the sample-spinning condition on a JEOL PS-100 high-resolution spectrometer at 100 MHz and 35.0°C ± 0.3°C. NMR samples were prepared as dilute $CDCl_3$ solutions (less than 1 mol%) with cyclohexane as internal reference. The proton chemical shifts δ (in Hz) at atmospheric pressure and at 1500 bar relative to the internal reference are listed in Table 1. The first thing to be noted is that the relative pressure shift $\delta\Delta$[6)] defined as $\delta(1500) - \delta(1)$ is positive, that is, to low field for the $H_{a,b}$ protons of ring B and the methylene protons. It is indicative of stronger association of these protons with the solvent $CDCl_3$ molecules under high pressure than that of cyclohexane protons. The relative pressure shifts of 4.4 and 4.7 Hz for the $H_{a,b}$ protons of 1 and 2, respectively, are slightly larger in magnitude than those for ordinary *p*-substituted benzenes, e.g. 3.5, 2.0, and 1.7 Hz for benzene, *p*-xylene, and 1,4-di-*tert*-butyl benzene, respectively.[7)] Thus, most of the down-field shift may be interpreted simply in terms of π-complexing of ring B with $CDCl_3$ strengthened by pressure. On the contrary, the H_x protons are appreciably displaced to high field by pressure, i.e. $\delta\Delta = -7.7$ and -9.1 Hz for 1 and 2, respectively. Up-field pressure shift has been observed also for the chloroform proton in aromatic solvents.$^{8)}$ This is apparently due to a change in solvent effects by pressure. However, such an interpretation does not hold for the present up-field shift in $CDCl_3$. There is, therefore, an imperative necessity for invoking other mechanisms responsible for the shift.

In a previous NMR study of macrocyclophanes at atmospheric pressure, we found that the resonance of the H_x protons of ring A occurs at high field.$^{5)}$ This up-field shift was ascribed to the transannular shielding effect by ring B preferring the "face" conformation. In going from 2 to 1, closer proximity between ring A and ring B and widening of the angle between rings B cause an increase of the transannular shielding effect, shifting the H_x protons of 1 to higher field than those of 2. Reduction of the partial volumes of the present cyclophanes under high pressure can be effected by changes in the dihedral angles between the bonds connecting rings A and B and the concomitant proximity among the aromatic rings.$^{9)}$ For mutual orientations of rings A and B, the contraction may be regarded as tantamount to a change from 2 to 1. Therefore, the H_x protons shift to higher field and the $H_{a,b}$ protons to lower field. Subtracting the ordinary pressure shift of ~2 Hz from the observed pressure shifts, one may evaluate the pressure shift originating from intramolecular pressure effects. The decreased absolute values of the pressure shift for 1 compared with 2 are ascribable to the reduced flexibility of the whole molecule, which is evidenced by the temperature dependence of the chemical shifts for these cyclophane systems.$^{10)}$

References and Notes

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4) 1 was prepared by a coupling reaction between 1,4-bis(mercaptomethyl)benzene and bis(*p*-chloromethylphenyl)methane under high dilution conditions:5) mp 244.0-244.5°C; NMR ($CDCl_3$, 31.5°C) δ 3.56 (4H, s, $-CH_2S-$), 3.74 (4H, s, $-CH_2S-$), 3.82 (2H, s, $-CH_2-$), 5.96 (4H, s, H_x), 7.16 (8H, s, $H_{a,b}$); IR (KBr) 1510, 1420, 1110, 780, 600 cm^{-1}; mass spectrum *m/e* (rel intensity) 363 (12), 362 (M^+, 52), 195 (100), 91 (42). Anal. Calcd. for $C_{23}H_{22}S_2$: C, 76.19; H, 6.12. Found: C, 76.16; H, 6.04.

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