1346 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1346—1347 (1971) [Vol. 44, No. 5

Conformational Changes in Heterocyclic Analogs of Metaparacyclophane

Sadatoshi AKABORI, Kengo SHIOMI, and Takeo SATO*
Department of Chemistry, Faculty of Science, Toho University, Narashino-shi, Chiba
**Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagayaku, Tokyo*

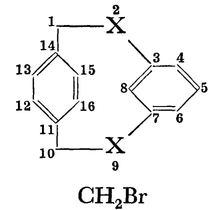
(Received October 2, 1970)

Sulfur analogs of [2.2]metaparacyclophane, II, III, and IV were prepared and their NMR spectra were examined. Of the three possible inversion mechanism, the one which involves the inversion of the *m*-phenylene unit is proposed.

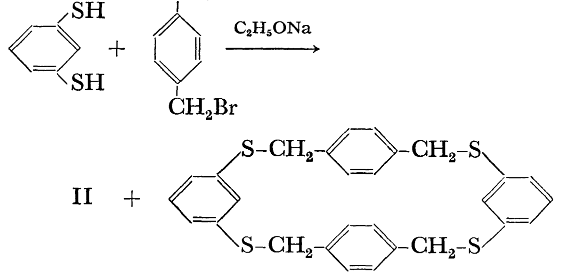
The unique features of [2.2]metaparacyclophane (I) system[1-5] resulting from the crowding of two aromatic rings give rise to interesting physical and chemical properties. They include anomalies in the ultraviolet[4] and nuclear magnetic resonance spectrum.[3,5]

In a paper[2] dealing with the NMR spectra of I, it was shown that inversion of the 11-membered ring occurred at temperatures higher than 187°C. In order to study the inversion mechanism further, 2,9-dithia[2.2]metaparacyclophane (II) and its derivative III were prepared and their NMR spectra were examined.

Compound II was prepared according to the procedure of Vögtle[3] by the reaction of *m*-benzenedithiol with 1,4-bis(bromomethyl)benzene under high dilution conditions. A colorless amorphous compound, mp 99—100°C was obtained. A 22-membered tetrathia compound IV[6] was isolated in 3.4% yield by the condensation between two moles each of the halide and the dithiol. When the reaction was carried out in THF only IV was formed even under high-dilution conditions.



	X
I	CH_2
II	S
III	SO_2



IV

The NMR spectrum[7] of II in CCl_4-CS_2 (1:1) at room temperature shows absorptions at δ 5.73 and 7.39 (broad signal, A_2B_2 pattern, $C_{12,13}$ and $C_{15,16}$ aryl protons), δ 6.90—7.40 (AB_2 pattern, $C_{4,5,6}$ aryl protons), δ 6.22 (triplet, C_8 aryl proton) and at δ 3.87 and 3.90 (broad absorption, AB pattern, methylene protons). The spectrum was essentially similar to that of Vögtle.[3] The C_8 and half-side of *p*-phenylene aryl protons exhibited unusual high field shifts due to the ring current effects of the opposite benzene ring. No such upfield shift was observed with the larger ring compound IV, which in DMSO-d_6 showed absorptions at δ 4.06 (singlet, methylene protons), δ 7.00 (singlet, *p*-phenylene unit aryl protons), δ 7.10 and 7.20 (AB_2 pattern, outer *m*-phenylene protons) and at δ 7.39 (inner *m*-phenylene protons). The peak for methylene protons of compound IV was a sharp singlet, which suggests that the comformation of cyclic compound is flexible, with no fixation.

Oxidation of II with 30% hydrogen peroxide in acetic acid gave III as colorless high-melting needles.

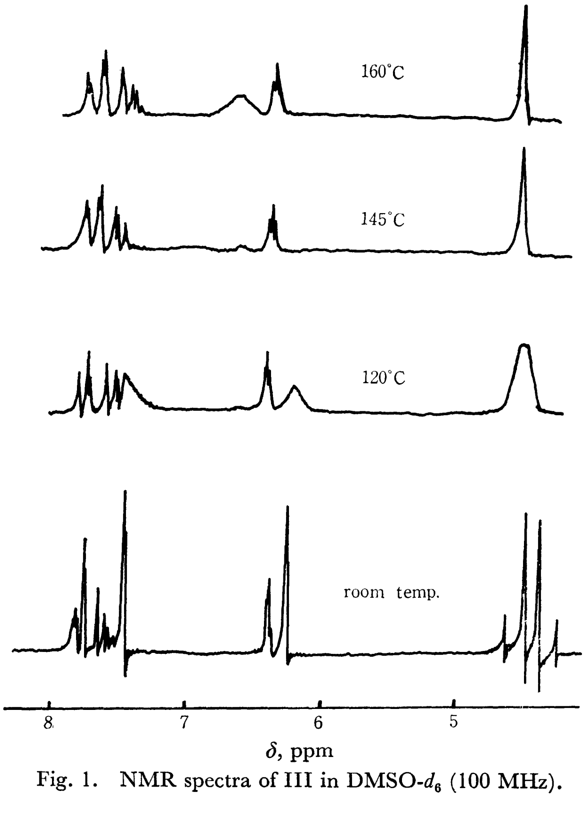


Fig. 1. NMR spectra of III in DMSO-d_6 (100 MHz).

---

1) T. Hylton and V. Boekelheide, *J. Amer. Chem. Soc.*, **90**, 6887 (1968).

2) S. Akabori, S. Hayashi, M. Nawa, and K. Shiomi, *Tetrahedron Lett.*, **1969**, 3727.

3) F. Vögtle, *Chem. Ber.*, **102**, 3077 (1969).

4) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Amer. Chem. Soc.*, **88**, 1324 (1966).

5) D. T. Hefelfinger and D. J. Cram, *ibid.*, **92**, 1073 (1970).

6) Parent peak, *m/e* 488. The spectrum was recorded on a Hitachi RMU-6 spectrometer.

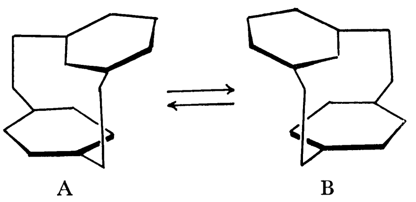
7) The spectra were recorded on a JNM-4H-100 spectrometer TMS as a reference.

8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

The structure was supported by elemental analysis and spectral data. As shown in Fig. 1, the NMR spectrum of III in DMSO-d_6 shows absorptions at δ 7.50 and 7.82 (AB_2 pattern, $C_{4,5,6}$ aryl protons), δ 6.28 and 7.48 (A_2B_2 pattern, $C_{12,13,15,16}$ aryl protons), δ 6.40 (triplet, C_8 aryl proton) and at δ 4.34 and 4.54 (AB pattern, $J=13$ Hz, methylene protons). Downfield shift (0.18 ppm) of C_8 aryl proton of III compared with that of II could be attributed mainly to the anisotropy effects of two sulfone groups. With the rise of temperature of the solution individual signals of A_2B_2 pattern collapse to a broad signal at about 145°C as shown in Fig. 1.

Temperature dependence of the A_2B_2 pattern is in line with the exchange between $C_{12,13}$ and $C_{15,16}$ proton environments resulting from the ring inversion among conformers A and B. Based on the chemical shift at 23°C ($\Delta\nu=120$ Hz) and temperature of coalescence ($T_c=145$°C), the energy barrier to interconversion is calculated to be $\Delta G_c^{\ddagger}=20.0\pm0.3$ kcal/mol.[8,9] Inversion energy was calculated to be $\Delta G_c^{\ddagger}=20.1\pm0.4$ kcal/mol from methylene proton signals ($T_c=118$°C, $\Delta\nu=20$ Hz). The energy barrier for II,[10] however, was found to be as low as $\Delta G_c^{\ddagger}=14.8\pm0.4$ kcal/mol (calculated from methylene protons, $\Delta\nu=20$ Hz, $T_c=23.0$°C).[10] The difference is attributable mainly to the bulkiness and rigidness of sulfone groups as compared with bivalent sulfur groups.

There are three types of possible inversion mechanisms, (a), (b), and (c). In (a), inversion of the m-phenylene ring occurs through the rotation of C_1–C_2 and C_9–C_{10} bonds. In (b), rotation of p-phenylene unit occurs similarly about C_1–C_{14} and C_{10}–C_{11} bonds. In (c), rotation of the meta-ring occurs in a concerted fashion. Examination of molecular model[11] of I indicates that the para-ring is more strained that the meta-ring and inversion of the latter occurs more easily. By similar consideration (c) can be ruled out by steric hindrance of internal aryl protons. If the inversion was due to (b), one might not expect the coalescence of methylene protons of II and III at higher temperatures. At higher temperatures, however, II and III showed a sharp singlet due to methylene protons and a downfield shift of C_8 aryl protons. This suggests that the inversion may occur by (a).



Experimental

2,9-Dithia[2.2]metaparacyclophane (II). 1, 4-Bis(bromomethyl)benzene in 250 m*l* of dried tetrahydrofuran and solution of 7.1 g (0.05 mol) of m-benzenedithiol in 250 m*l* of 75% ethanol containing 5 g of sodium hydroxide were added separately drop by drop through a modified Hershberg dropping funnel to 1.5 *l* refluxing ethanol during the course of 48 hr. Stirring was carried out throughly during the addition. When it was complete, the resulting mixture was filtered for removal of sodium bromide. The filtrate was dissolved in benzene, washed with water. The benzene solution was then dried, concentrated and subjected to column chromatography on alumina using benzene as an eluent. From the first elute a colorless solid was isolated. By recrystallization from chloroform-benzene II was obtained in a 6.9% yield, mp 99—100°C, lit,[3] 99—100°C.

Found: C, 68.50; H, 4.64; S, 26.45%. Calcd for $C_{14}H_{12}S_2$: C, 68.85; H, 4.83; S, 26.27%.

From the second elute IV was isolated. It was recrystallized from chloroform to give 0.25 g (3.4% yield) of colorless solid, mp 218—220°C.

Found: C, 68.32; H, 4.88; S, 26.50%. Calcd for $C_{28}H_{24}S_4$: C, 68.85; H, 4.83; S, 26.27%.

When a solution of 10 g (0.07 mol) of m-benzenedithiol in 320 m*l* absolute ethanol containing 5 g of sodium hydroxide and a solution of 18.5 g (0.07 mol) of 1,4-bis(bromomethyl)-benzene in 320 m*l* of dried tetrahydrofuran were added to 200 m*l* of tetrahydrofuran in the course of 98 hr at room temperature. A 5.7% yield of IV, mp 218—220°C, was obtained.

2,9-Dithia[2.2]metaparacyclophane-2,2,9,9-tetroxide(III). A mixture of 2.25 g of II dissolved in 30 m*l* glacial acetic acid containing 30% hydrogen peroxide was put to stand at room temperature overnight. It was concentrated *in vacuo* to give white crystals, which were dissolved in chloroform and subjected to silica gel column chromatography using chloroform as an eluent. Compound III was obtained as colorless needles, recrystallized from chloroform, mp >300°C, in an 8% yield, $\nu_{\max}$ 1310 and 1150 cm^{-1}.

Found: C, 54.67; H, 3.76%. Calcd for $C_{14}H_{12}S_2O_4$: C, 54.55; H, 3.92%.

We wish to thank the Ministry of Education for financial support.

---

[9] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, Inc., London, 1941, Chapt. 1.

[10] In Ref. 3, a value of $\Delta G_c^{\ddagger}$ was calculated as 14.7 kcal/mol based on the aryl protons of A_2B_2 pattern and as 14.9 kcal/mol based on the methylene signals of AB pattern.

[11] R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).