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HETERA-p-CARBOPHANES. V. EFFECT OF OXYGENATION OF SULFUR ON THE ROTATIONAL BARRIER IN A THIAPARACYCLOPHANE DERIVATIVE [1)]

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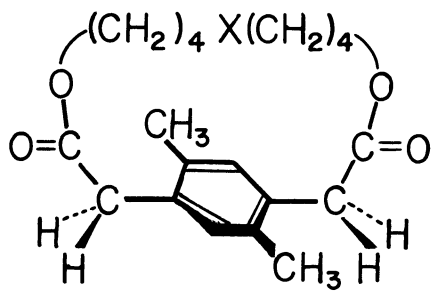
Dynamic nuclear magnetic resonance study of 17,20-dimethyl-3,13-dioxa-8-thia-2,14-dioxo[15]paracyclophane and its oxygenated derivatives revealed that the barrier to rotation of the aromatic ring increased in the order of sulfide < sulfoxide < sulfone. Transannular interaction of the charge transfer type is discussed as a possible cause for the change in barriers.

During the course of study on the relationship between the structure and the rotational barrier of the hetera-p-carbophane, we have come across an interesting phenomenon. Namely, oxygenation of the sulfur atom in 17,20-dimethyl-3,13-dioxa-8-thia-2,14-dioxo[15]paracyclophane (2) was found to produce a significant increase in the barrier to rotation of the aromatic ring. We wish to present the finding and to discuss the possible origin of the increase in the barrier.

17,20-Dimethyl-3,13-dioxa-8-thia-2,14-dioxo[15]paracyclophane (2), mp 70-71°C, was prepared by condensation between 5-thianonane-1,9-diol and 2,5-dimethyl-1,4-phenylenediacetyl dichloride under high dilution conditions as reported previously.[2)] The corresponding sulfoxide (3) mp 134.0-134.5°C, and sulfone (4), mp 123-124°C, were prepared by oxidation of the sulfide 2 with sodium metaperiodate in aqueous methanol-acetone and hydrogen peroxide in acetic acid, respectively. These compounds gave satisfactory analytical and spectral results.

The benzylic protons of these compounds showed AB quartet signals at room temperature, whereas they coalesced into singlets on raising the temperature. The free energies of activation for rotation of the aromatic ring were calculated using the coalescence temperatures, chemical shift differences, and coupling constants[3)]



(1): X = CH_2
(2): X = S
(3): X = SO
(4): X = SO_2

and the results are listed in Table 1, together with the corresponding data of 17,20-dimethyl-3,13-dioxa-2,14-dioxo[15]paracyclophane (1) for comparison. The free energy of activation for rotation of the aromatic ring in 1 in hexachlorobutadiene had been reported[2] but that in dimethyl-d_6 sulfoxide was determined again because the oxygenated sulfur compounds were not sufficiently soluble in hexachlorobutadiene for determination of the PMR spectra.

Table 1 PMR Data (60 MHz) and Free Energies of Activation for Internal Rotation of Paracyclophane Derivatives

X	$\Delta\delta$ (Hz)	J_{AB} (Hz)	Tc (°C)	$\Delta G_c^{\ddagger}$ (kcal/mol)	Solvent
CH_2	16.7	13.6	189	23.3	hexachlorobutadiene
	14.1	14.4	188	23.3	dimethyl sulfoxide
S	14.6	14.0	130	20.3	hexachlorobutadiene
	10.0	14.0	109	19.2	dimethyl sulfoxide
SO	9.0	14.6	160	21.8	dimethyl sulfoxide
SO_2	10.8	14.5	166	22.1	dimethyl sulfoxide

Comparison of the $\Delta G_c^{\ddagger}$'s in Table 1 reveals that the barrier to rotation is the highest for compound 1 and that those of the sulfur compounds are lower. Close examination of the data indicates that the barrier is heightened when the sulfur carries oxygen atom(s). Although the errors included in the calculation of the free energies will amount to ±0.2 kcal/mol, the tendency is clearly seen from the data.

In discussion of the barriers to rotation, one has to take both the ground

state and the transition state into accounts. The higher barrier of compound 1 is apparently caused by shorter bond lengths of the C-C (1.54 Å) relative to that of the C-S (1.80 Å). That is, the transition state is more crowded in compound 1 than those in sulfur compounds.

However, the change in barriers in compounds 3 and 4 on going from compound 2 cannot be attributed to the change in transition states. Bond lengths and bond angles of a sulfide, a sulfoxide, and a sulfone were collected from various sources in Table 2. It will be seen that the bond lengths and bond angles are, by and large, the same.

Table 2 Interatomic Distances and Bond Angles in Dimethyl Sulfide and Its Oxygenated Derivatives

Compound	C-S (Å)	∠CSC (°)	Literature
CH_3SCH_3	1.805	101.2	4)
CH_3SOCH_3	1.798	97.4	5)
	1.807	97.86	6)
$CH_3SO_2CH_3$	1.770	102.5	7)
	1.778	103.0	8)

A preliminary calculation of the Urey-Bradley force field,[9] using the same force constant for the deformations of $CS(O)_nC$ and assuming that the methyl group is a particle, gave a fairly good agreement between the observed and the calculated spectra for dimethyl sulfide, dimethyl sulfoxide, and dimethyl sulfone. Thus the ease of angle deformation in sulfides, sulfoxides, and sulfones may not differ much from each other.

Now it becomes reasonable to assume that the ground states of the oxygenated sulfur compounds are stabilized to some extent relative to that of compound 2. Sulfur trioxide and sulfonyl compounds carrying electronegative groups such as sulfuryl chloride are known to act as Lewis acids. Likewise, thionyl chloride acts as an acid and even sulfur dioxide is known to complex with alkenes.[10] It may not be unreasonable to assume that, as an extention of the above facts, sulfoxides and sulfones can accept electrons from the π-base to form charge-transfer complexes, although the interaction may be weak. This supposition is

consistent with a fact that mixing aromatic hydrocarbons with dimethyl sulfoxide is less endothermic than the case of aliphatic saturated hydrocarbons.[11] Then, as in the case of rotation in biphenyl derivatives,[12] the stabilization of the ground state should raise the barrier to rotation.

The reason why this sort of weak interaction is detected must be the crowdedness of the molecule. The steric conditions are such that the oxygenated sulfur is closely located above the benzene ring and fixed fairly rigidly at the site. Detection of such an interaction by other means is now under investigation.

A similar phenomenon has been reported with metacyclophane derivatives.[13] However, the reason for this phenomenon may be different from the one discussed here, because the steric situation is not favorable for the interaction to take place in this series of compounds.

References

1) Part IV: K. Sakamoto and M. Ōki, submitted for publication in Bull. Chem. Soc. Jap.
2) K. Sakamoto and M. Ōki, submitted for publication in Bull. Chem. Soc. Jap.
3) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York (1959), p. 218; J. W. Emsley, J. E. Feeney, and C. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford (1965), p. 481.
4) S. Tsuchiya, K. Otaki, and M. Kimura presented before the 30th meeting of the Chemical Society of Japan at Higashi-Osaka, April 1974, Abstract, Vol. 1. p. 116.
5) R. Thomas, C. B. Shoemaker, and K. Eriks, Acta Crystallogr., 21, 12 (1966).
6) M. A. Wiswamitra and K. K. Kannan, Nature, 209, 1016 (1966).
7) H. Oberhammer and W. Zeil, J. Mol. Struct., 6, 399 (1970).
8) D. E. Sands, Z. Kristallogr., 119, 245 (1963).
9) K. Fujimori, Bull. Chem. Soc. Jap., 32, 1374 (1959).
10) P. W. Jones and A. H. Adelman, Tetrahedron, 30, 2053 (1974) and papers cited therein.
11) C. V. Krishnan and H. L. Friedman, J. Phys. Chem., 73, 1572 (1969); ibid., 75, 3598 (1971).
12) M. Ōki, K. Akashi, G. Yamamoto, and H. Iwamura, Bull. Chem. Soc. Jap., 44, 1683 (1971).
13) T. Sato, M. Wakabayashi, M. Kainosho, and K. Hata, Tetrahedron Lett., 1968, 4185; T. Sato, M. Wakabayashi, K. Hata, and M. Kainosho, Tetrahedron, 27, 2737 (1971).

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