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RESTRICTED ROTATION AROUND THE ARYL TO SULFINE BOND IN MESITYL SUBSTITUTED SULFINES[1]

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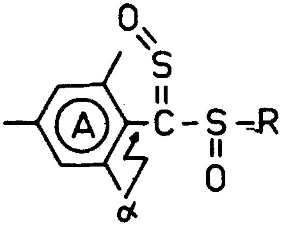
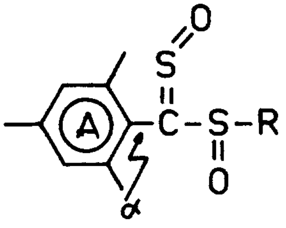
An interesting series of substituted sulfines was recently prepared by stepwise oxidation of dithiocarboxylic esters with peroxyacids[2], e.g. phenyl 2,4,6-trimethyldithiobenzoate gave mesityl phenylthio-, mesityl phenylsulfinyl-, and mesityl phenylsulfonyl-sulfines, respectively.

It was found[2] that the *ortho* methyl protons in the sulfoxide sulfine I $(R=C_6H_5)$ as well as in its geometrical isomer II $(R=C_6H_5)$ appear as different signals in the NMR spectrum[3]. This magnetic non-equivalence must be due to the presence of the pyramidal asymmetric sulfoxide function, which condition, however, is not sufficient. Application of Mislow's test[4] for diastereotopic groups implies that the *ortho* methyl groups only become diastereotopic, when interchange of the *ortho* methyl groups by rotation around the aryl to sulfine bond (α) which is a twofold axis of symmetry for these groups, is slow on the NMR time scale. When rotation around bond α becomes fast, the basic requirement[5] for the *ortho* methyl groups being diastereotopic is no longer fulfilled, with the consequence that the methyl groups become equivalent. Hence, variable temperature NMR analysis of these compounds provides a means to determine the rotational barrier in the aryl to sulfine bond α. Coalescence of the two methyl



I (*E*-isomer)



II (*Z*-isomer)

signals to one singlet was indeed observed for the sulfoxide sulfines I and II at elevated temperatures. The results are listed in the Table[6]. During this NMR analysis no Z to E (or visa versa) isomerization was observed.

TABLE

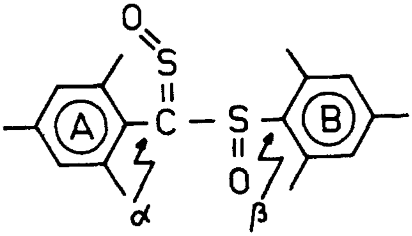
	$\Delta\nu$ in Hz ($^{\circ}$C)	T_c in $^{\circ}$C	$\Delta G_c^{\ddagger}$ in kcal/mole
E-series I			
Ia ethyl	2.7 (32°)*	130	22.4
Ib phenyl	31 (105°)**	195	23.9
Ic α-thienyl	15 (32°)**	180	23.7
Id β-naphthyl	34 (105°)**	197	23.9
Ie mesityl	α :25 (105°)**	230	25.9
	β :74.8 (32°)**	94	17.9
Z-series II			
IIb phenyl	98 (32°)*	130	19.5
IIc α-thienyl	63.4 (32°)*	139	19.1
IId β-naphthyl	109 (32°)*	115	19.7

$\Delta\nu$: difference in chemical shift between ortho methyl groups obtained at 100 Mhz (varian HA-100).
Solvent: * nitrobenzene; ** m-dinitrobenzene
$\Delta G_c^{\ddagger}$: calculated with Eyring's formula; the listed values are ± 0.3 kcal/mole

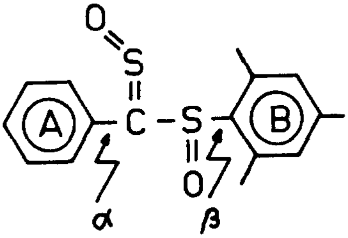
The $\Delta G_c^{\ddagger}$-values show that the rotational barrier for bond α in the Z-series is smaller than in the E-series. This observation most likely reflects the difference in spatial position of the sulfine oxygen: a higher $\Delta G_c^{\ddagger}$ will result when the oxygen is situated between the two ortho methyl groups as is the case in the E-series. For the geometrical isomers of ortho substituted N-nitrosoanilines a comparable influence of the geometry was encountered[7].

The presented data also show that in the E-series the barrier to rotation is only slightly affected by the substituent R for R being phenyl, α-thienyl, and β-naphthyl. For R being the less bulky aliphatic ethyl group the $\Delta G_c^{\ddagger}$-value is about 1.5 kcal/mole less.

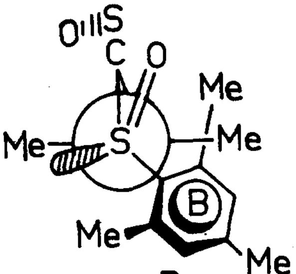
An interesting observation was made for the mesityl mesitylsulfinyl sulfine Ie. At room temperature six different methyl absorptions were found which point to two barriers of rotation, viz. around bond α and around the sulfoxide to mesityl bond (β). Strikingly, no restricted rotation was observed (at 25 °C) when the mesityl ring A was replaced by a phenyl group, i.e. sulfine III6). This means that restricted rotation around bond β does not simply involve steric interactions of the ortho methyl groups in the B-ring and the sulfoxide function, but that the A-part of the molecule plays a decisive role. Presumably, a preferred folded conformation P in which there is a considerable steric interaction between one ortho methyl of the B-ring and one of the A-ring, must be taken into account.



Ie



III

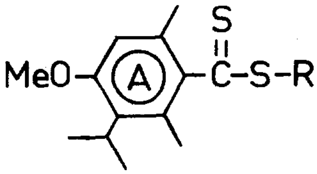


P

This influence is mutual, as is expressed in the higher $\Delta G_c^{\ddagger}$-value for rotation around bond α in Ie as compared with Ib.

In the E-series of these sulfoxide sulfines the $\Delta G_c^{\ddagger}$-values are of suitable magnitude to allow the separation of diastereomers, when the A-ring bears any substituent in the meta position.

For comparison the rotational barrier for the parent dithiocarboxylic esters were desired. In order to do so, a diastereotopic marker was introduced



	$\Delta\nu^{*}$	T_c	$\Delta G_c^{\ddagger}$
IVa	4.2 Hz (32°)	69 °C	18.6 kcal/mole
IVb	2.5 Hz (32°)	52 °C	18.0 kcal/mole

* between Me signals of the iPr group, solvent nitrobenzene

IVa : R = phenyl
IVb : R = β -naphthyl

in the A-ring, *viz*. a *meta* isopropyl group (IV). Non-equivalence of the methyl groups within the isopropyl group is only possible8) when rotation around the aryl to thione bond is restricted. The $\Delta G^{\ddagger}_{T_c}$-values reveal that for these esters the rotation barrier is smaller than for the *Z* sulfoxide sulfines, which is most likely due to secondary effects such as conformational and structural differences. The introduction of a *meta* isopropyl group will enable us to measure also rotation barriers for the other types of sulfines derived from dithio esters, namely arylthio- and arylsulfonyl-sulfines.

Acknowledgement:

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REFERENCES AND NOTES

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2. B. Zwanenburg, L. Thijs and J. Strating, *Rec. Trav. Chim*. *90*, 614 (1971).
3. Also the *meta* protons of the mesityl ring show up as two different signals.
4. K. Mislow and M. Raban in "Topics in stereochemistry", Ed. N.L. Allinger and E.L. Eliel, John Wiley, New York, 1967, vol I, chapter 1.
5. Unfortunately, we did not point explicitly to this basic requirement in our previous paper (ref. 2).
6. The new sulfines Ia, c, d, e, IIc, d, and III were prepared by oxidation of the corresponding dithioesters as described in ref. 2.
7. A. Mannschreck and H. Muensch, *Tetrahedron Letters*, *1968*, 3227.
8. An example of a compound which produces non-equivalence of the X-groups in an $A-CX_2-B$ system, where either A or B is asymmetric4).