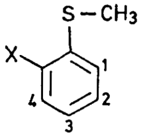
Conformational Dependence of Long-range Coupling in *ortho*-Substituted Thioanisoles

By L. LUNAZZI*
(*University of Bologna, Institute of Organic and Industrial Chemistry, Viale Risorgimento, 4, 40136 Bologna, Italy*)
and D. MACCIANTELLI
(*Laboratorio dei composti del carbonio contenenti eteroatomi, C.N.R., Ozzano Emilia, Italy*)

Summary The variation of ^5J in the title compounds with temperature and the size of the substituents has been interpreted as depending on the population of the *anti*-configuration.

WE have observed the existence of long-range coupling constants (^5J) through the sulphur atom in *ortho*-substituted thioanisoles:



The couplings occur between the hydrogens of the SCH_3 group and the hydrogen in the *ortho*-position (1-H), as is shown by a computer analysis of the spectrum of *o*-bromothioanisole (X = Br) which gives the following results:

$\nu_1 = 417{\cdot}427$, $\nu_2 = 427{\cdot}650$, $\nu_3 = 410{\cdot}728$, $\nu_4 = 443{\cdot}313$
$J_{1,2}$ 7·907, $J_{1,3}$ 1·572, $J_{1,4}$ 0·302, $J_{1,\text{Me}}$ 0·326, $J_{2,3}$ 7·401, $J_{2,4}$ 1·351, $J_{3,4}$ 7·929.

Spectra recorded at both 60 and 100 MHz confirm that the observed separations of the methyl doublet do represent the actual value of the coupling constant, and accordingly, the differences between the directly measured splitting and the computer best-fit lie within the limits of experimental error: for the observed spectra of *o*-bromothioanisole, $J_{\text{SMe-H}_o} = 0{\cdot}31 \pm 0{\cdot}01$ and $0{\cdot}32_6 \pm 0{\cdot}006$ Hz, respectively.

As previously reported for anisoles[1,2] the couplings can be detected only for sufficiently bulky *ortho*-substituents while, when X = H or NH_2, for instance, the SCH_3 gives a single signal.

In the case of the anisoles this was attributed to the steric effect of the bulky substituents upon the conformations of the methoxy-group; the preferred conformation being that with the OMe *"anti"* to the substituent in the *ortho* position. If this hypothesis is correct, the larger size of the sulphur atom would cause a greater dependence of the analogous $J_{\text{SMe-H}_o}$ on the size of X as well as on the temperature. The results are listed in the Table.

Coupling constants (Hz) between SCH_3 *and* ortho-*H in* ortho-*substituted thioanisoles*

Substituent	CH_3	Cl	$C(CH_3)_3$	Br	I	NO_2
^5J	0·13	0·17	0·25	0·31	0·36	0·43

Although there is no unambiguous method of measuring the steric hindrance, the van der Waals radius may reasonably be taken as an indication of such an effect; for substituents comprising more than one atom, the summation of these radii, as used in building up molecular models, was employed. For X = Me and Bu^t the average for the conformations with the greatest and smallest steric effects towards SCH_3 were used, whilst for X = NO_2 the conformation parallel to the benzene ring (which is likely to have the greatest statistical weight because of the conjugative power of the nitro-group[3]) was employed. It can be seen (Figure) that a regular dependence does exist between the size of the substituents, defined in such a way (Me: 1·68, Cl: 1·75, Br: 2·00, I: 2·15, NO_2: 2·55, CMe_3: 2·05), and the $J_{\text{SMe-H}_o}$; the greater the size of X, the greater is the statistical weight of the conformation with SCH_3 *"anti"* to the substituent and, therefore, the greater the value of the coupling. When X = OCH_3 and $N(CH_3)_2$ no coupling could be detected for the SCH_3, thus suggesting that the methoxy- and dimethylamino-groups (as opposed to the nitro) tend to retain conformations with minimum steric hindrance towards the SCH_3. This is further supported by the observation of $J_{\text{OMe-H}_o}$ 0·22 in *o*-methoxythioanisole.

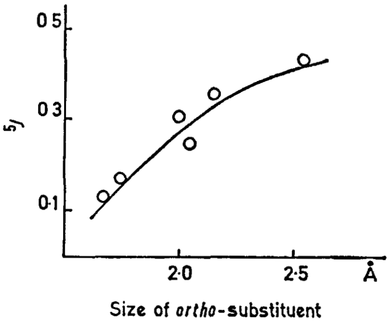


FIGURE. *Dependence of* ^{5}J *on the size of the* ortho-*substituent.*

At higher temperatures the $J_{\text{SMe-H}_o}$ of all the *ortho*-substituted thioanisoles is expected to diminish, since conformations with SCH_3 *"syn"* to the substituent become more populated than at room temperature. In two cases (*o*-nitro- and *o*-bromo-thioanisoles) the coupling was actually found to depend linearly on the temperature, with J values dropping from 0·43 to 0·30 and from 0·31 to 0·15 Hz, respectively, as the temperature was increased from 25° to 100°; this further supports the hypothesis of conformational dependence.

An interesting consequence of this interpretation is the possibility of predicting the preferred conformations of the corresponding *ortho*-substituted sulphoxides and sulphones. Their spectra give sharp lines (width $0{\cdot}2_5$ Hz) for the methyl group and do not exhibit appreciable coupling despite the fact that, on purely electronic grounds, they would be expected to show even greater coupling than is observed in the corresponding sulphides.[4] It seems reasonable to conclude that in hindered sulphoxides and sulphones the conformations with greater statistical weight are those with the methyl "*syn*" and the oxygen "*anti*" to the *ortho*-substituent.

One of us (L.L.) thanks Dr. R. J. Abraham, University of Liverpool, and Prof. F. Taddei, University of Modena, for helpful comments.

(*Received, April* 5*th*, 1971; *Com.* 493.)

[1] R. W. Crecely, K. W. McCracken, and J. H. Goldstein, *Tetrahedron*, 1969, **25**, 877.
[2] H. Angad Gaur, J. Vriend, and W. G. Huysmans, *Tetrahedron Letters*, 1969, 1999.
[3] "Steric effects in Organic Chemistry", ed. M. S. Newman, Wiley, New York, 1956, p. 651.
[4] N. Van Meurs, *Spectrochim. Acta*, 1963, **19**, 1695.