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ON THE ASSIGNMENT OF AZOTHIO-GROUP STRETCHING VIBRATIONS IN AZOTHIOBENZENES

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RECENTLY one of us (G.L.) described the preparation of azothio-benzenes, the sulphur-analogues of azoxybenzenes, by the action of sodium metal in boiling toluene solution on the corresponding thio-nylanilines;[1a] good evidence was obtained as to the proposed structure of the reaction products from their chemical reactivity[1a] and ultra-violet spectra.[1b]

From our knowledge,[2] there does not appear to be any specific infra-red study on organic molecules containing N-S bonds, owing perhaps also to the somewhat uncommon occurrence of such bonds. We give here briefly some relevant infra-red data pertaining mainly to the -NNS- part of our molecules, while a more detailed report on the infra-red work is being prepared for

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[1a] G. Leandri and P. Rebora, Experientia 13, 71 (1957); Gazz. Chim. Ital. 87, 503 (1957); b G. Leandri and A. Mangini, Boll. Sci. Fac. Chim. Ind. Bologna 15, 51 (1957).

[2] For reviews see L. J. Bellamy, The Infra-red Spectra of Complex Molecules, Chap.22. Methuen, London (1958); L.J. Bellamy, in Organic Sulphur Compounds, (Edited by N. Kharasch). Pergamon Press, New York (1959); J. Lecomte, in Handbuch der Physik, Band 26, Licht un Materie II, Chap.D.XX. Springer, Berlin (1958).

publication elsewhere.[3] The molecules examined are azothiobenzene $C_6H_5{-}N{=}\underset{S}{N}{-}C_6H_5$ and its $-Cl$, $-Br$, $-CH_3$, $-OCH_3$ and $-C_6H_5$ p-disubstituted derivatives. The spectra were recorded on a Perkin-Elmer Model 21 double-beam instrument with NaCl optics, for solutions in CCl_4, C_2Cl_4 and CS_2 and partly in the solid (as KBr pellets) and liquid state.

The general features of the spectra, as refers to the ring vibrations and to those pertaining to the substituent group, are as a whole in excellent agreement, both in position and intensity, with the recent detailed work by Maier and Englert[4] on azoxybenzenes, with a few noticeable exceptions to be discussed later;[3] such a behaviour strongly supports again the structure proposed for our molecules as azoxy-similar.

Referring now to the azothic-group symmetrical and asymmetrical stretching vibrations, their location may be foreseen, as a very rough approximation, on considering that: (a) the azoxy-group asymmetrical stretching vibration falls in the range 1450-1480 cm^{-1},[4] indicating that it partakes mainly the character of an $-N{=}N-$ stretching mode;[5] the same

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[3] A paper by the same authors, to be presented before the Meeting of European Molecular Spectroscopists, Bologna, Italy, 7-12 Sept. (1959).

[4] W. Maier and G. Englert, *Z. Elektrochem.* **62**, 1020 (1958); see also B. Witkop and H. M. Kissman, *J. Amer. Chem. Soc.* **75**, 1975 (1953); J. Jander and R. N. Haszeldine, *J. Chem. Soc.* 919 (1954).

[5] R. J. W. LeFèvre *et al.*, *Aust. J. Chem.* **6**, 341 (1953); **9**, 151 (1956); **10**, 26 (1957); **11**, 92 (1958); G. Costa, *Ann. Chim.* **46**, 649 (1956); D. Hadzi, *J. Chem. Soc.* 2143 (1956); R. Mecke and E. Greinacher, *Z. Elektrochem* **61**, 530 (1957); K. Ueno, *J. Amer. Chem. Soc.* **79**, 3205 (1957); as to the effect of hydrogen bonding on $-N{=}N-$ stretching in formazans see A. Foffani, C. Pecile and S. Ghersetti, *Tetrahedron Letters* No. 11, 16, (1959).

should essentially be valid for the corresponding azothio- stretching mode, to be expected falling therefore around the same region; (b) also the azoxy-symmetrical stretching is found,[4] fairly unsensitive to structural effects, in the sharp range 1315-1335 cm^{-1}, namely in a position not far from that (1200-1300 cm^{-1}) normally observed for the stretching mode of N-O bond in N-oxides;[6] by comparing now for example the mean location[2] of C=O and C=S stretching vibrations, from the mean ratio $\nu_{C=O}/\nu_{C=S} = 1.1+1.6$ it is reasonable, by simple mass effect, to expect finding the azothio-group symmetrical stretching mode in the region 900-1100 cm^{-1}.

Looking now to the spectra, it is easily observed (for details see ref. 3) that indeed in the suspected regions, and only there, two strong bands are present which cannot reasonably be identified as ring- or substituent-group-vibrations. Their approximate position is as follows: azothiobenzene (AT) 1070, 1448; p,p'-di-chloro-AT 1063, 1459; p,p'-dibromo-AT 1058, 1458; p,p'-dimethyl-AT 1062, 1448; p,p'-dimethoxy-AT 1068, 1463; p,p'-diphenyl-AT 1070, 1448 cm^{-1}.

The high intensity of the bands and the great similarity of their form from compound to compound supports well their belonging to fundamental stretching modes of the central part of the molecules; the experimental ranges are therefore 1065±6 cm^{-1} for the asymmetrical vibration. We are careful however to point out that in the lack of further information,

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[6] G. Costa *et al.*, *Gazz. Chim. Ital.* **85**, 1085 (1955); *Z. Phys. Chem. Neue Folge* **4**, 24 (1955); **7**, 123 (1956); R. H. Wiley and S. C. Slaymaker, *J. Amer. Chem. Soc.* **79**, 2233 (1957); A. R. Katritzky *et al.*, *J. Chem. Soc.* 2182, 2192, 2195 (1958); for quinoline N-oxides see A. Foffani, G. Favaro and A. Risaliti, Unpublished results.

particularly of measurements in polarized light on oriented samples,[4] some degree of uncertainty surely remains in our present tentative assignments; this is especially true, as discussed,[3] for the asymmetrical mode, which falls near to a ring vibration and in some cases cannot unequivocally be distinguished from it.