1. Kjær, A. and Thomsen, H. *Acta Chem. Scand.* **16** (1962) 591.
2. Christensen, B. W. and Kjær, A. *Acta Chem. Scand.* **16** (1962) 2466.
3. Kjær, A. *Fortschr. Chem. org. Naturstoffe* **18** (1960) 122.

Received December 22, 1962.

Long-range Proton Spin Couplings in Thieno[3,2-b] thiophene

BO GESTBLOM

Institute of Physics, University of Uppsala, Uppsala, Sweden

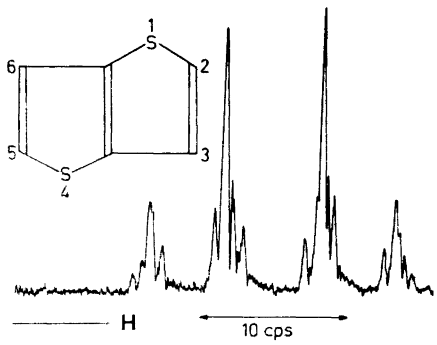

Fig. 1.

In connection with the investigation of the ring-closure of some α-[thienylthio] substituted acids [1], the NMR-spectrum of thieno[3,2-b] thiophene has been studied. At low resolution it appears as an AB spectrum, but at higher resolution additional fine structure is seen revealing the presence of cross-ring couplings giving an A_2B_2 pattern [2]. A complete analysis of the spectrum gave the following coupling constants; $J = +5.30$ cps, $J' = -0.20$ cps, $J_A = +1.50$ cps and $J_B = +0.75$ cps.

$J = J_{23} = J_{56}$ is of the same order as in thiophene [3] and is arbitrarily chosen positive. $J' = J_{26} = J_{35}$ is over five bonds and is small ,while J_A and J_B are over five and six bonds and are unexpectedly large. Out of the A_2B_2 analysis it is impossible to determine which diagonal coupling is J_A and which J_B. J_{36} is over five bonds while J_{25} is over six bonds which might lead to the conclusion that J_{36} is the largest. The recent suggestion [4] of largest coupling through the "straightest zig-zag path" also supports this assignment. Results obtained for a structurally similar compound, N-benzylthieno [3,2-b]pyrrole [5], however supports the opposite assignment. There [5] it was found that the cross-ring coupling over six bonds between the α-hydrogens is the largest (1.3 cps), more than twice the corresponding β coupling (0.5 cps). Any cross-ring couplings between the α and β hydrogens were not observable.

In analysing the A_2B_2 spectrum it is possible to take advantage of the fact that the rough shape of the spectrum is that of an AB quartet showing that the cross-ring couplings are much smaller than the AB coupling. In A_2B_2 spectra the energy levels can be calculated in closed form except for the S_0 levels which are obtained from a 4×4 matrix [2]. Now, instead of choosing the base functions of this submatrix as the products of the base functions for A_2 and B_2 of appropriate symmetry, it is in the present case suitable to choose as base functions the products of the AB eigenfunctions of correct symmetry. This leads to the approximate diagonalization of this submatrix making the off-diagonal elements small compared with the corresponding diagonal element differences. For sufficiently small off-diagonal elements, that is small J', J_A and J_B, it would thus be accurate enough to use only first order perturbation theory. With this treatment all expressions for the transition frequencies and intensities are given in closed form. Aslo for not too large off-diagonal elements, it may suffice to go to second order perturbation theory.

Five parameters, the relative shift ($\nu_0\delta$) and four coupling constants had to be determined by comparison of calculated spectra with the observed one. Good values of $\nu_0\delta$ and the largest coupling J were immediately obtainable by disregarding the fine structure and treating the spectrum as an AB case. The three remaining couplings were then simultaneously varied and promising assignments closer investigated. The method of Dischler and Maier [6] was also used to test calculated assignments, and several were found to fulfill the criteria given by these authors. However only the one here reported gave a calculated spectrum in agreement with the measured one. This assignment was also checked by exact diagonalization.

The compound was studied in different solvents and at both 40 Mcps and 60 Mcps to vary $\nu_0\delta$ and thus check the fit of the assignment of couplings for different spectra. The spectrum shown was recorded in an 11.7 % solution in acetone at 60 Mcps giving $\nu_0\delta = 10.80$ cps.

The method of analysing A_2B_2 spectra presented here is thus appliable when the spectrum can be regarded as a perturbed AB case and should then be useful. A more extensive discussion with applications to other compounds will be published later.

I wish to express my thanks to Professor Kai Siegbahn for his interest in this work, to Dr. R. A. Hoffman for valuable discussions and hints and to Dr. S. Gronowitz for supplying the compound.

1. Gronowitz, S., Rudén, U. and Gestblom, B. *Arkiv Kemi. In press.*
2. Pople, J. A., Schneider, W. G. and Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance.* New York 1959.
3. Hoffman, R. A. and Gronowitz, S. *Arkiv Kemi* **15** (1959) 45.
4. Banwell, C. N. and Sheppard, N. *Paper presented at the discussion on high-resolution NMR of the Faraday Society,* Oxford 1962.
5. Tuite, R. J., Snyder, H. R., Porte, A. L. and Gutowsky, H. S. *J. Phys. Chem.* **65** (1961) 187.
6. Dischler, B. and Maier, N. *Z. Naturforsch.* **16a** (1961) 318.

Received January 8, 1962.

Partial Characterization of the Hydrocarbons of Herring Oil

GEORG LAMBERTSEN and RALPH T. HOLMAN

Hormel Institute, University of Minnesota, Austin, Minnesota, U.S.A.

Shark liver oils are known to contain high concentrations of hydrocarbons, and squalene is present in as high as 80 % of the oil of the basking shark. Other well characterized hydrocarbons in fish oils are pristane and zamene, belonging to the C_{19} aliphatic terpenoids [1,2]. Others have been named, but their structures are uncertain [3].

A preliminary gas chromatographic study of several vegetable oils and fish oils revealed the presence of complicated mixtures of hydrocarbons in many of them. In general the vegetable oils contained fewer hydrocarbons than did the fish oils. Rape seed oil contained several major hydrocarbon constituents, whereas squalene was the principal hydrocarbon in olive oil.

Herring oil was studied in most detail. This oil contained 0.05 % hydrocarbons, about 5 % of the unsaponifiable matter. 500 g of herring oil were saponified [4] using hydroquinone and ascorbic acid as antioxidants. The unsaponifiable fraction was extracted quickly with ethyl ether and resaponified. The unsaponifiable fraction was chromatographed on alumina with hexane and the eluate was concentrated and rechromatographed in the same way on a smaller column. Upon evaporation of the solvent, the fraction gave a near-infrared spectrum corresponding to a pure hydrocarbon.

Table 1. Hydrocarbons occurring in herring oil as determined by gas chromatography.

Straight chain components		Branched chain components	
Carbon Number	% area	Carbon Number	% area
14.0	0.3	15.4	3.5
15.0	7.5		
16.0	0.6	16.8 (pristane)	70.0
17.0	9.0		
17.6	2.2	17.9	5.0
18.0	1.7		
19.0	10.5	19.0	0.5
20.0	0.3		
21.0	6.0	19.9	1.0
22.0	0.3		
23.0	0.8	~21*	3.5
24.0	0.3		
25.0	9.5	22.2	3.5
26.0	trace		
27.0	33.0	26.3 (squalane)	13.0
28.0	trace		
29.0	9.0		
30.0	trace		
31.0	~7		
32.0	(trace)		
33.0	~1		

* Flat and broad peak.