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APPLICATIONS OF NMR SPECTROSCOPY IN THE FIELD OF POLYCONDENSED AROMATIC SYSTEMS

IX—TRI AND TETRACYCLIC DERIVATIVES OF CHROMONE, 1-THIOCHROMONE, XANTHEN-9-ONE, THIOXANTHEN-9-ONE AND RELATED STRUCTURES[1,2]

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Abstract—*Ortho and peri* effects due to cyclic heteroatoms and (thio)carbonyl functions have been compared in the (1-thio)chromone and (thio)xanthen-9-one series.

As a result of this work, the 7H-benzo[c]thioxanthen-7-one structure XVI has been assigned to the benzothioxanthone first isolated by Davis and Smiles,[3] and the 12H-benzo[b]thioxanthen-12-one structure XVII has been assigned to a new compound synthesized as part of this study. IR spectroscopy has been used to provide certain supplementary information.

Résumé—Les effets *ortho* et *péri* dûs aux hétéroatomes cycliques et aux fonctions (thio)carbonyles ont été comparés dans la série des (1-thio)chromones et des (thio)xanthén-9-ones.

L'étude du spectre RMN de la benzothioxanthone, isolée pour la première fois par Davis et Smiles,[3] permet d'attribuer à ce dérivé la structure 7H-benzo[c]thioxanthén-7-one XVI.

La structure d'un composé tétracyclique nouveau, la 12H-benzo[b]thioxanthen-12-one XVII, a été confirmée par spectroscopie RMN.

Certaines données de spectroscopie infra-rouge complètent ce travail.

IN THE course of previous work, we have shown that NMR spectroscopy can often be used to elucidate the structure of cyclic ketones resulting from the cyclization of γ-arylbutyric acids (aryl = polycyclic aromatic hydrocarbon radical).[4]

The present investigation was undertaken in order to see if similar results could be obtained in the case of heterocyclic ketones and thioketones. It was therefore decided to examine the NMR spectra of the tetracyclic derivative (m.p. 196–197°) prepared by the condensation of thiosalicylic acid with naphthalene in the presence of sulphuric acid, a reaction which could give either A, B, C or D (Fig. 1).

Davis and Smiles,[3] who first isolated this condensation product (reported m.p. 186°), made no attempt to elucidate its structure but, in 1938, Knapp[5] synthesized A (reported m.p. 193–194°) by an unambiguous procedure.

[1] Part I: R. H. Martin, *Tetrahedron* **20**, 897 (1964).

[2] Part VIII: R. H. Martin, J. P. Van Trappen, N. Defay and J. F. W. McOmie, *Tetrahedron* **20**, 2373 (1964).

[3] E. G. Davis and S. Smiles, *J. Chem. Soc.* **97**, 1290 (1910).

[4] R. H. Martin, N. Defay and F. Geerts-Evrard, *Tetrahedron* **20**, 1505 (1964).

[5] W. Knapp, *Monatsh. Chem.* **71**, 440 (1938).

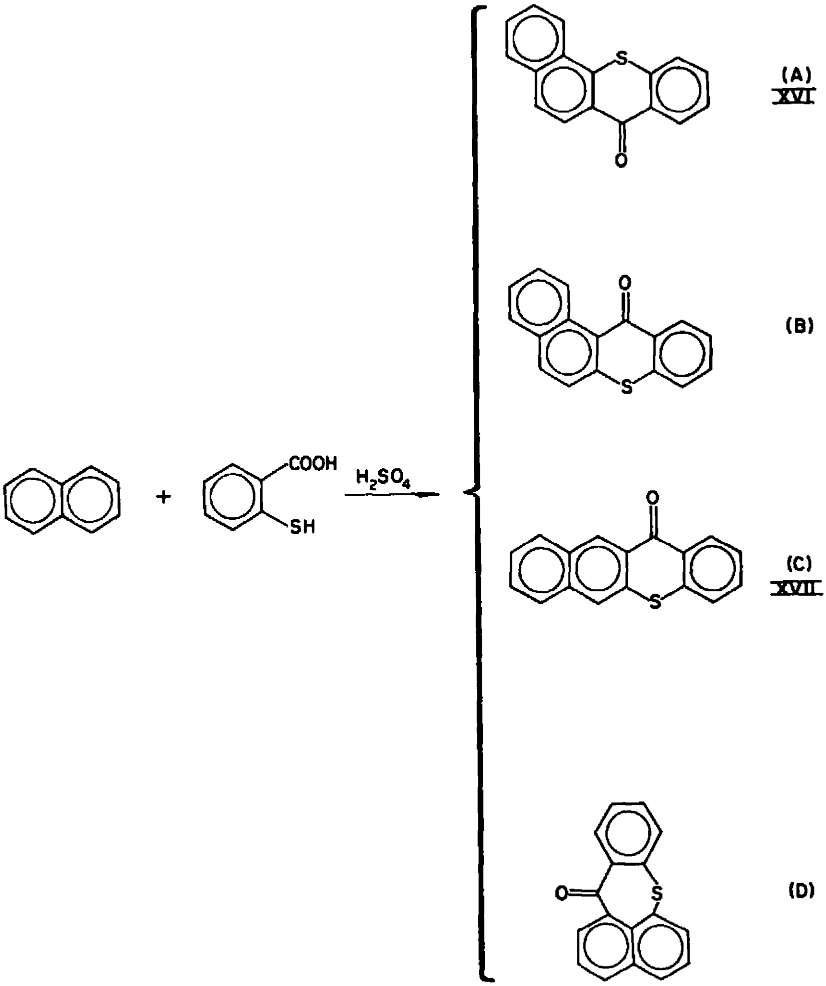

Fig. 1

When the first NMR spectrum of the unknown tetracyclic compound was recorded, it was at once apparent that only structure A is compatible with the observed NMR pattern.

Subsequent extensive work on model substances, which are now described, confirm the 7H-benzo[c]thioxanthen-7-one structure (A) deduced from the NMR spectrum. Moreover, C has been synthesized and is a different compound.

The hitherto unreported 12H-benzo[b]thioxanthen-12-one (C) has been prepared by the condensation of 3-mercapto-2-naphthoic acid with benzene in the presence of sulphuric acid. Any benzothioxanthone resulting from this reaction would be the C isomer, but the reaction in fact yields a mixture of substances, and it was not clear that the single substance isolated in a state of purity is in fact the 12H-benzo[b]thioxanthen-12-one. The NMR spectrum by itself and when compared with the spectra of the model substances is consistent with the view that the substance obtained (m.p. 236·5°) has the structure XVII.

General discussion

The spectra described in this paper were recorded on an A60 (60 Mc) VARIAN spectrograph. The $CDCl_3$ solutions were either of the order of 8% (w/v) or, for the very insoluble derivatives, saturated solutions at 25°. The spectra are represented diagrammatically in Figs. 2 and 5. All the compounds used in this work with the exception of xanthen-9-thione III, thioxanthen-9-thione V, 1H-naphtho[2,1-b]pyran-1-one XIV and 4H-naphtho[1,2-b]pyran-4-one XV, which were prepared by one of us (F. G. E.) in Brussels, were synthesized in the American laboratory.

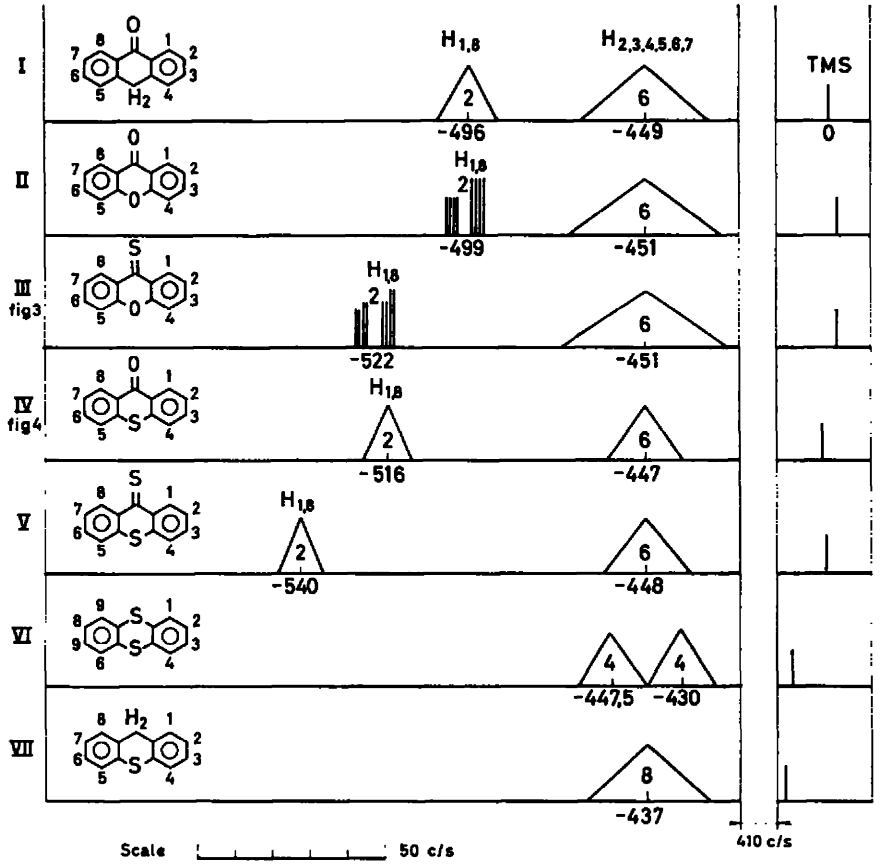

FIG. 2. Diagrammatic representation of NMR spectra* of xanthan-9-one, thioxanthen-9-one and related structures: benzenoid protons.

* Chemical shifts are reported to the estimated center of the multiplets and expressed in c/s at 60 Mc (internal reference TMS = O, solvent: $CDCl_3$). The J values were simply measured on the spectra. The center of the multiplets corresponding to "unperturbed protons" are arbitrarily aligned.

Chemical shifts of the non-benzenoid protons: I CH_2 (s) −251; VII CH_2 (s) −230. J values: II $J_{1,2}$ = 7·4, $J_{1,3}$ = 2, $J_{1,4}$ = 0·8; III $J_{1,2}$ = 8, $J_{1,3}$ = 1·7, $J_{1,4}$ = 0·7.

The NMR spectra of xanthen-9-one (II) and chromone have been recently recorded and calculated by Mathis and Goldstein.[6]

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[6] C. T. Mathis and J. H. Goldstein, *Spectrochim. Acta* **20**, 871 (1964).

1. *Xanthen-9-ones and Thioxanthen-9-ones* (Fig. 2)

The following observations are of interest with regard to this series of compounds.

1.1 "*Unperturbed protons*"

In the heterocyclic ketones (II and IV) and thioketones (III and V) the chemical shift of the "unperturbed protons" is very similar to that of the corresponding protons in anthrone (I) (−449 c/s). The aromatic protons of thioxanthene (VII) give rise to a complex set of signals centred at −437 c/s.

TABLE 1. DESHIELDING* IN *ortho* (H_1 AND H_8) TO THE CARBONYL AND THIOCARBONYL FUNCTIONS ($CDCl_3$)

Position 10	Position 9	
	>C=O	>C=S
—CH₂—	I −47	
—O—	II −48	III −71
—S—	IV −68	V −92

* The values represent the difference in chemical shift between the "perturbed protons" and the "unperturbed protons" (estimated centre of the multiplet) of the same molecule.

1.2 *Influence of the cyclic carbonyl and thiocarbonyl function*

Ortho Effects (Table 1). H_1 and H_8 are deshielded by the presence, in the *ortho* position, of a cyclic carbonyl or thiocarbonyl function. This deshielding is largest in the thioketones ($\delta_{C=S} - \delta_{C=O} \sim 23$ c/s).

In both series, the deshielding varies with the nature of the central ring:*

$$CH_2 , O < S$$

2. *Chromone and* 1-*Thiochromone Derivatives* (Fig. 5).

2.1 *Protons located in the neighbourhood of the carbonyl function*

2.1.1—*ortho* and *peri* Effects (Table 2). In 1-thiochromanone IX and 1-thiochromone X (Fig. 6), the deshielding of the benzenoid proton (H_5), *ortho* to the carbonyl function, is greater than the deshielding of the corresponding protons in chromone (H_5) and in 1-oxo-1,2,3,4-tetrahydronaphthalene VIII (H_8).

On the other hand, in the corresponding tricyclic derivatives (XI, XII, XIII and XIV), the *peri* deshielding effect is only slightly larger in 1H-naphtho[2,1-b]thiopyran-1-one XIII (Fig. 7) than in 1H-naphtho[2,1-b]pyran-1-one XIV and the smallest effect is observed in XII.

2.1.2—*ortho* and *peri* Deshielding effects are both larger in the 1-thiochromone (X) and 1H-naphtho[2,1-b]thiopyran-1-one (XIII) than in the corresponding 2,3-dihydro-derivatives (IX and XII; Table 2).

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* The same deshielding is apparent in the spectrum of acridone recorded in DMS by J. P. Kokko and J. H. Goldstein, *Spectr. Chim. Act.* **19**, 1119 (1963).

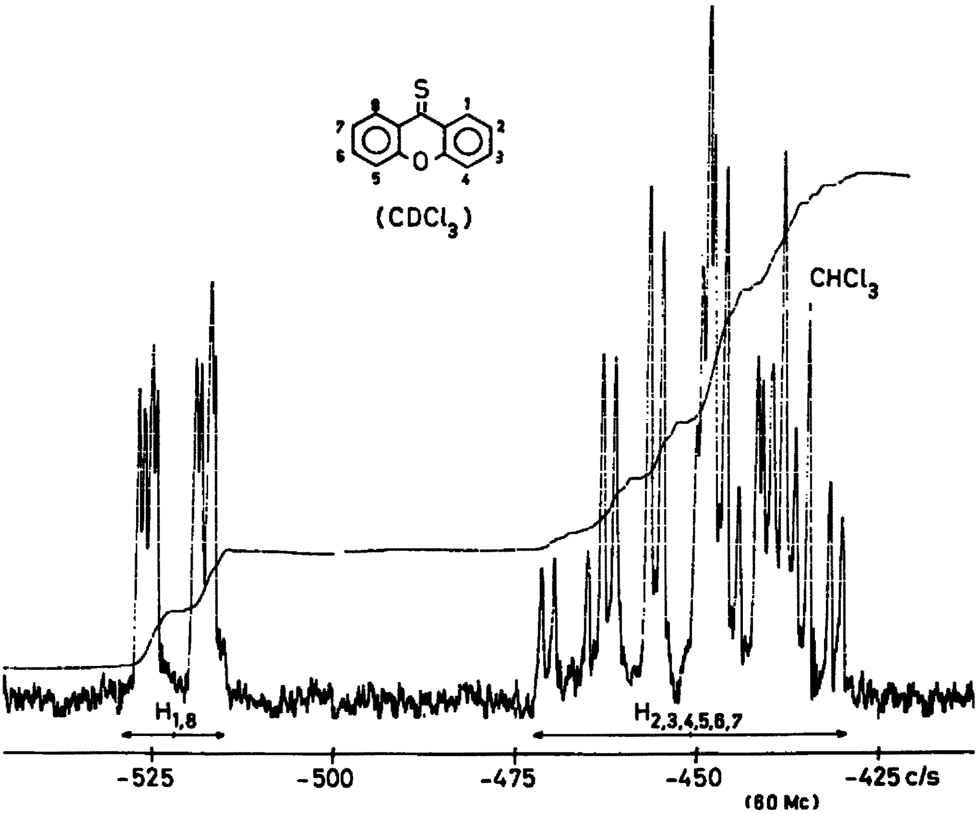
S
8
1
7
2
6
3
O
5
4
(CDCl$_3$)
CHCl$_3$
H$_{1,8}$
H$_{2,3,4,5,6,7}$
-525
-500
-475
-450
-425 c/s
(60 Mc)

FIG. 3

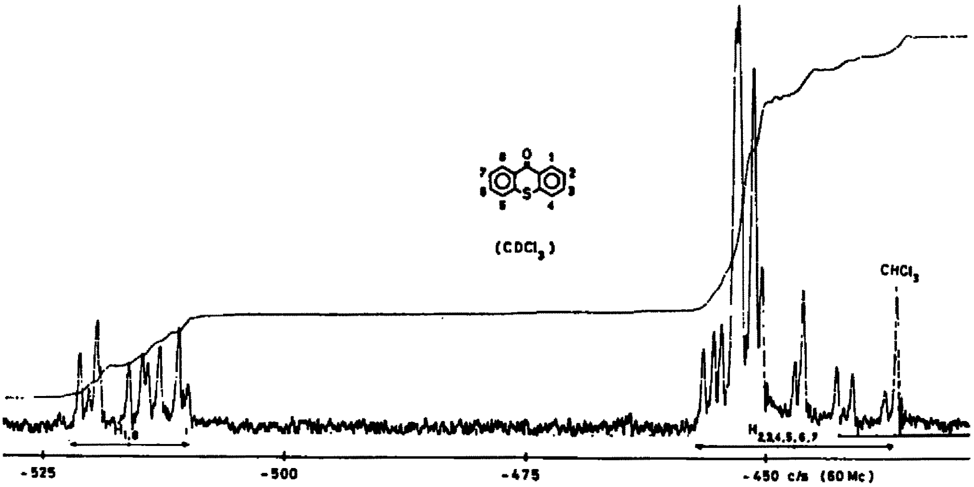
O
8
1
7
2
6
3
S
5
4
(CDCl$_3$)
CHCl$_3$
H$_{1,8}$
H$_{2,3,4,5,6,7}$
-525
-500
-475
-450 c/s (60 Mc)

FIG. 4

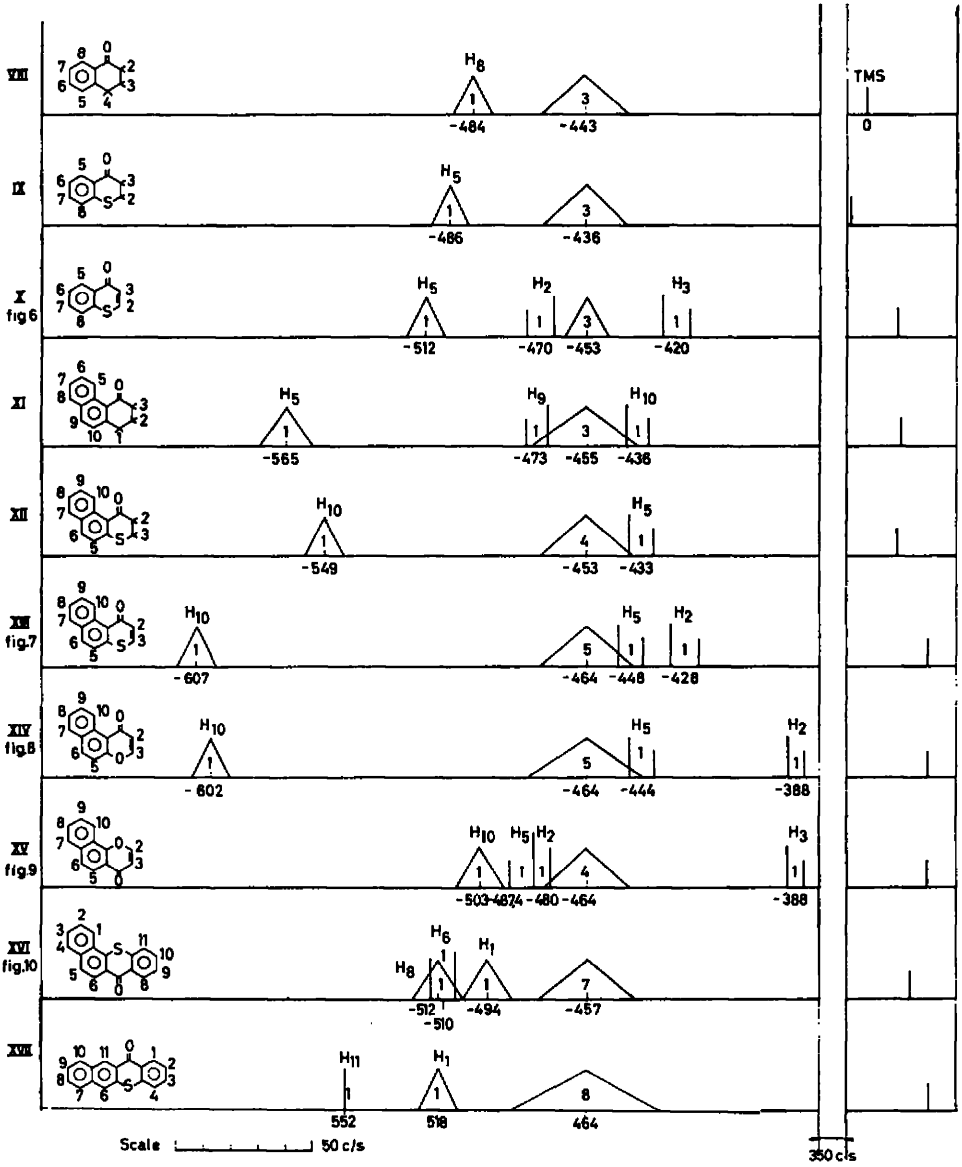

FIG. 5. Diagrammatic representation of NMR spectra* of chromone and 1-thiochromone derivatives and related structures: benzenoid protons.

Chemical shifts of the non-benzenoid protons: IX CH$_2$ in 2 and 3 (m) −186; XII CH$_2$ in 2 and 3 (m) −188; VIII and XI see Ref. 4. J values: X $J_{2,3}$ = 10·5; XII $J_{5,6}$ = 8·7; XIII $J_{2,3}$ = 10·4, $J_{5,6}$ = 8·9; XIV $J_{2,3}$ = 5·9, $J_{5,6}$ = 8·9; XV $J_{2,3}$ = 6, $J_{5,6}$ = 8·8; XVI $J_{5,6}$ = 8·7.

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* See footnote Fig. 2.

These results were expected in view of the fact that in the 1-thiochromones the carbonyl function is more rigidly held in the vicinity of the perturbed protons.

The structural differences between the reduced and the more conjugated ring systems are also reflected in the fact that in the latter, the multiplet structure of the "unperturbed protons" is shifted to lower field.

TABLE 2. DESHIELDING* OF BENZENOID PROTONS *ortho* OR *peri* TO THE CARBONYL FUNCTION

Ring A	*Ortho*	*Peri*
—CH_2—	VIII H_5 −41	XI H_5 −110
—S—	IX H_5 −50	XII H_{10} − 96
—S—	X H_5 −59	XIII H_{10} −143
—O—	† H_5 −40	XIV H_{10} −138

* See footnote Table 1.

† Chromone see Ref 6.

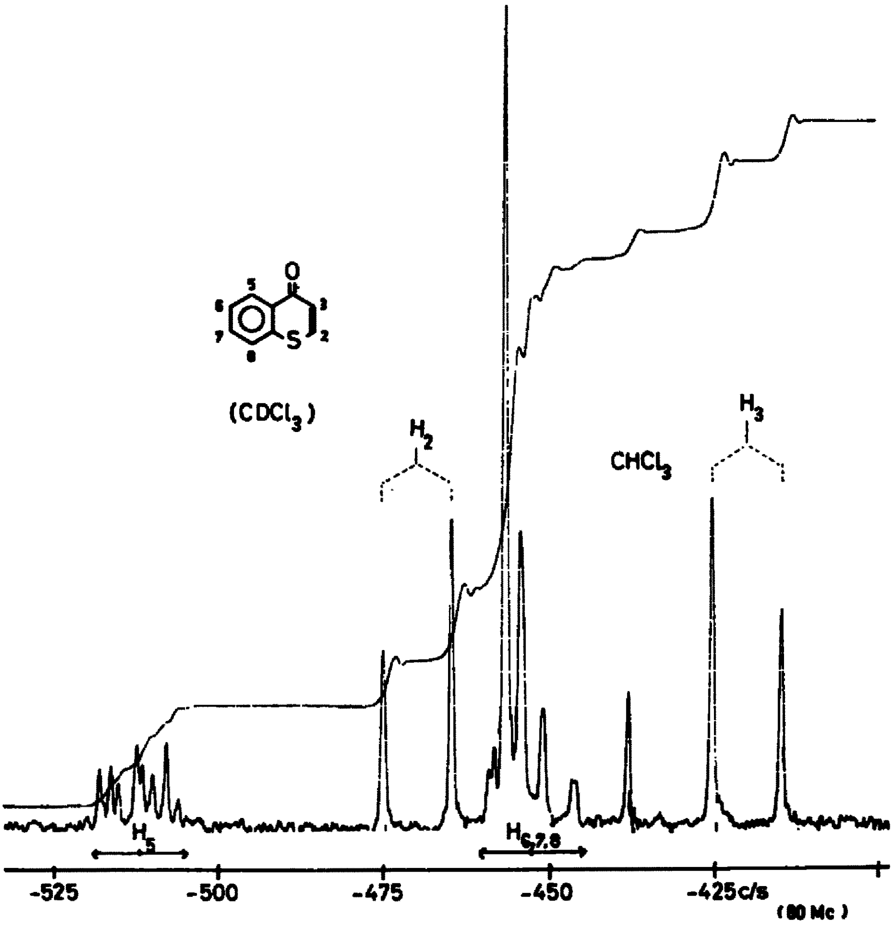

FIG. 6

2.1.3 The non-benzenoid protons, α to the carbonyl function, are found at higher field in the chromones than in the corresponding 1-thiochromones and the J values are much larger in the latter (Table 3).

TABLE 3. CHEMICAL SHIFTS* OF NON-BENZENOID PROTONS α TO THE CARBONYL FUNCTION IN CHROMONES AND 1-THIOCHROMONES ($CDCl_3$)

—O—	†	H_3 −380·4	$J_{2,3} = 6·05$
—O—	XIV	H_2 −388	$J_{2,3} = 5·9$
—O—	XV	H_3 −388	$J_{2,3} = 6·0$
—S—	X	H_3 −420	$J_{2,3} = 10·5$
—S—	XIII	H_3 −428	$J_{2,3} = 10·4$

* c/s at 60 Mc (TMS = 0) see footnote Fig. 2.
† Chromone see Ref. 6.

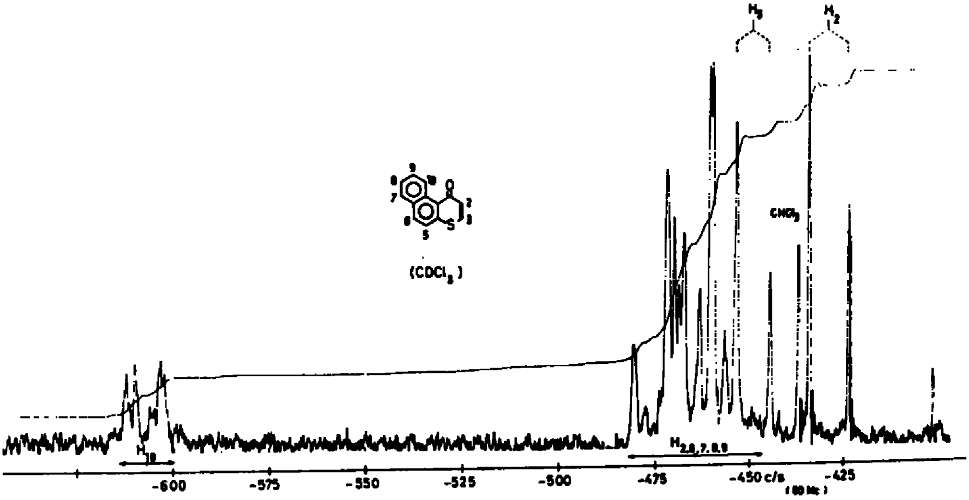

FIG. 7*

2.2 *Protons located in the neighbourhood of the cyclic oxygen and sulphur atoms* (Table 4)

Benzenoid protons *ortho* to the cyclic heteroatoms are shielded and in the 4H-naphtho[1,2-b]pyran-4-one (XV) the proton *peri* to the cyclic heteroatom is deshielded. This *peri* deshielding effect is also apparent in the spectrum of the tetracyclic thiopyrone (XVI).

TABLE 4. SHIELDING AND DESHIELDING* OF BENZENOID PROTONS *ortho* OR *peri* TO THE CYCLIC HETEROATOM

Ring A	*ortho*	*peri*
—S—	XIII H_6 +16	XVI H_1 −37
—O—	XIV H_5 +20	XV H_{10} −39

* See footnote Table 1.

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* In Figs 7 and 8 $\xleftrightarrow{H_{2\cdot6\cdot7\cdot8\cdot9}}$ should read $\xleftrightarrow{H_{3\cdot6\cdot7\cdot8\cdot9}}$

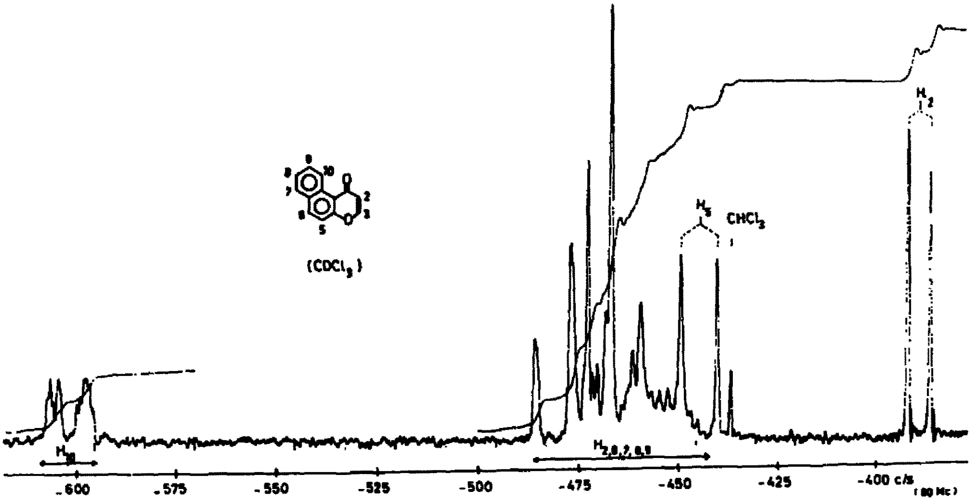

FIG. 8*

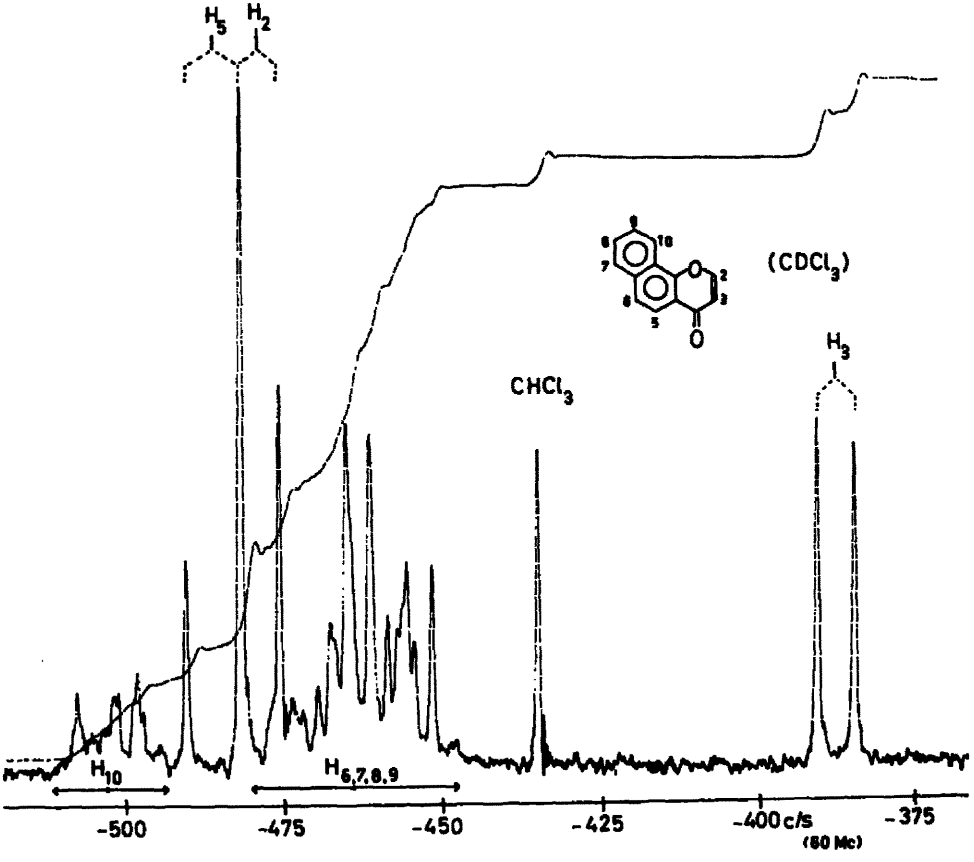

FIG. 9

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* See footnote p. 1840

2.3 *Spectra of the isomeric naphthopyrone* XIV *and* XV (*Figs.* 8 *and* 9)

These spectra show considerable differences.

In XIV H_{10} is very strongly deshielded (—138 c/s) because of the *peri* effect of the carbonyl function.

In XV the *peri* deshielding effect, due to the cyclic oxygen atom, is much smaller (—39 c/s).

In XIV, H_5 is shielded (+20 c/s) by the cyclic oxygen (*ortho* effect), while in XV, H_5 is deshielded (—23 c/s) by the carbonyl function (*ortho* effect).

3. *Structure of the Benzothioxanthone* (*m.p.* 196–197°) *prepared according to the Method of Davis and Smiles*[3]

The NMR spectrum (Fig. 10) of XVI shows a large multiplet structure (7H) centred at —457 c/s and three deshielded protons centred respectively at —512 c/s (—54 c/s, multiplet), —510 c/s (—52 c/s, doublet) and —494 c/s (—37 c/s, multiplet).

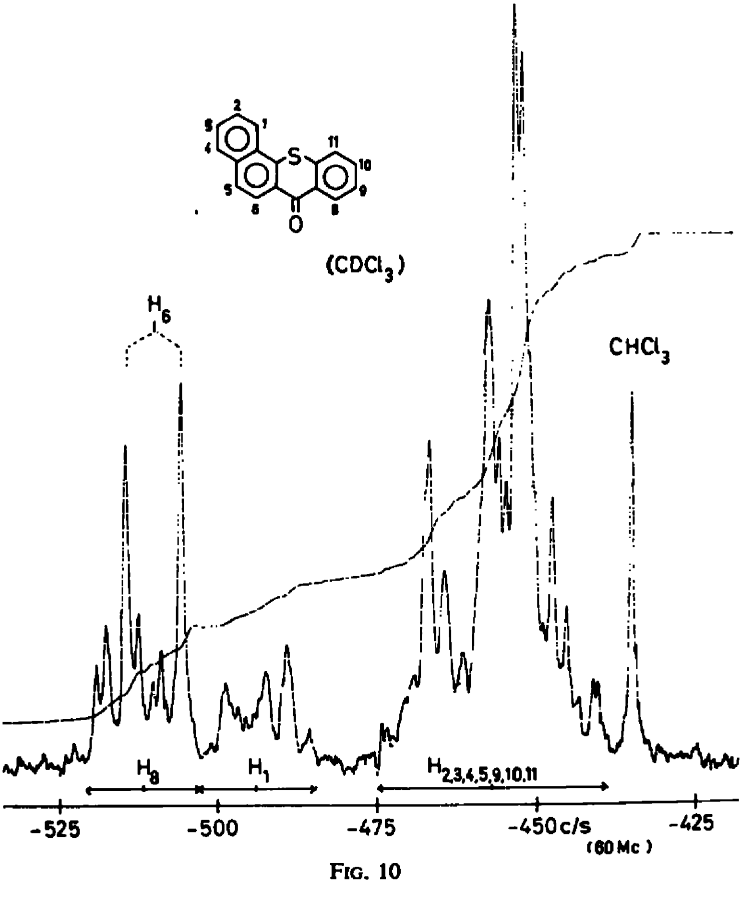


FIG. 10

This pattern excludes structures B, C and D (Fig. 1) for the following reasons: The absence of a very strongly deshielded proton excludes structure B, in which H_1 should experience the *peri* effect (>100 c/s) of the carbonyl group.

In structures C and D a maximum of two protons would be deshielded.

On the other hand, structure A is fully compatible with the observed NMR spectrum, for H_6 and H_8 should experience an *ortho* deshielding effect (C=O), similar to that observed in thioxanthen-9-one (−68 c/s) and H_1 a *peri* deshielding effect (—S—) which may be expected to be of comparable magnitude to that due to the cyclic oxygen in 4H-naphtho[1,2-b]pyran-4-one XV (−39 c/s).

On account of the above considerations, the following attributions can be made with confidence: H_8 multiplet at −512 c/s, H_6 doublet at −510 c/s and H_1 multiplet at −494 c/s. We therefore arrive at the conclusion that the benzothioxanthone, first described by Davis and Smiles,[3] is in fact 7H-benzo[c]thioxanthen-7-one (A). A direct comparison between this compound and Knapp's "3,4-benzothioxanthone" is therefore highly desirable.

4. *Structure of the Benzothioxanthone (m.p. 236, 5°) prepared from 3-Mercapto-2-naphthoic Acid*

The NMR spectrum of XVII shows a large multiplet structure centred at −464 c/s ($H_{2,3,4,6,7,8,9,10}$), a smaller multiplet centred at −518 c/s (H_1) and a one proton singlet at −552 c/s (H_{11}). This pattern confirms the 12H-benzo[b]thioxanthen-12-one structure.

5. *Correlation with IR Spectroscopic Data*

Two points of interest arise from a comparison of IR and NMR data.

The carbonyl vibrations of the 4-thiopyrone derivatives occur at relatively low frequencies, as might be expected. In the two cases where comparison is possible, the carbonyl frequency of the sulphur compound is some 20 cm^{-1} lower than that of its oxygen analogue. It is very noticeable that those cyclic ketones (XIII and XIV) that have a proton (H_{10}) in the *peri* position to the carbonyl have exceptionally low carbonyl frequencies. At the same time the H_{10} proton is very highly deshielded, and the chemical shifts (10·1 and 10·03 ppm respectively) are even higher than those of the protons in aldehydes. There may be a common explanation of the two phenomena, but it is not easy to see what this is. The observed carbonyl frequencies are listed in Table 5.

The second point of interest is that the aromatic C—H bending vibrations in the IR spectra of the two benzothioxanthones confirm the skeletal structures assigned. These vibrations are diagnostic of the type of substitution on the benzene ring. There is a close correspondence between the main C—H stretching bands of the angular 7H-benzo[c]thioxanthen-7-one and those of benzo[a]anthraquinone, which has the same skeletal structure, and also between the bands of the linear 12H-benzo[b]thioxanthen-12-one and naphthacenequinone. The principal frequencies are compared in Table 6; weak bands are omitted, and of the stronger bands the less important are in parentheses.

The bands at 730–770 cm^{-1} are undoubtedly associated with "end-ring" absorption, that is, with four adjacent hydrogen atoms; the assignment of the bands at 709 and 712 cm^{-1} in the spectra of the quinones is not clear and the bands are not present in the spectra of the parent hydrocarbons. The absorptions at 820–860 cm^{-1} in the spectra of the two angular four-ring compounds must be assigned to the presence of two adjacent free hydrogen atoms (1,2,3,4-tetrasubstitution). Similarly, the absorption around 900 cm^{-1} in the spectra of the linear four-ring compounds presumably arises from the two hydrogen atoms in the 1,2,4,5-substituted ring; the frequency

TABLE 5. CARBONYL FREQUENCIES OF OXYGEN AND SULPHUR ANALOGUES (MEASURED IN KBr DISCS)

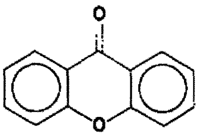
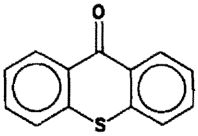
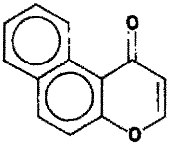
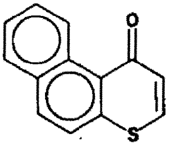
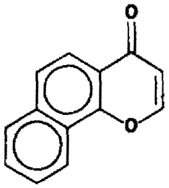
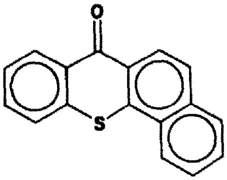
O-compound	$\bar{\nu}$, cm^{-1}	S-compound	$\bar{\nu}$, cm^{-1}
II 	1667	IV 	1640
XIV 	1638	XIII 	1616
XV 	1660	—	
—		XVI 	1629

TABLE 6. C—H BENDING VIBRATION OF BENZOTHIOXANTHONES AND RELATED QUINONES

Substance	Frequency, cm^{-1}	
7H-benzo[c]thioxanthen-7-one	(861), (853), 828	745, 736
Benzo[a]anthraquinone	842	767, 757, 709
12H-benzo[b]thioxanthen-12-one	(920), 875	750, 741
Naphthacenequinone	924	753, 712

range usually given for two hydrogens in the *para*-position to one another is 860–900 cm^{-1} (it is 890 cm^{-1} in naphthacene), so that it is apparently elevated somewhat by the presence of carbonyl.

EXPERIMENTAL

7H-*Benzo*[c]*thioxanthen*-7-*one* (XVI). This condensation product was prepared essentially by the procedure of Davis and Smiles.[6] These authors report that a bis-condensation product is formed as a by-product. Since we had difficulty in removing the by-product by crystallization, the crude material was separated by chromatography from benzene solution on alumina, and the desired product was eluted with ether. It was finally purified by crystallization from ethylene dichloride (m.p. 196–197°). (Found: S, 12·25. Calc. for $C_{17}H_{10}OS$: S, 12·22%).

The bis-condensation product was eluted with chloroform. After recrystallizations from ethylene dichloride it had m.p. 331–333°.

12H-*Benzo*[b]*thioxanthen*-12-*one* (XVII). 3-Mercapto-2-naphthoic acid was prepared from 3-amino-2-naphthoic acid by a procedure given in the literature[7] for the conversion of anthranilic acid to thiosalicylic acid. The product after crystallization from alcohol–water and alcohol–benzene had m.p. 300–305° (dec) (lit. value[8] 276°).

The mercapto acid was condensed with benzene in the presence of sulphuric acid, following the procedure of Davis and Smiles[6] for thioxanthen-9-one. The product was crystallized from alcohol (and separated from a quantity of slightly soluble material) and from methylcyclohexane; m.p. 236·5°. (Found: C, 77·4; H, 4·7; O, 6·1; S, 12·1. Calc. for $C_{17}H_{10}OS$; C, 77·85; H, 3·82; O, 6·11; S, 12·22%).

Thioxanthen-9-one (IV). This was made by the condensation of thiosalicylic acid with benzene in sulphuric acid, following Davis and Smiles procedure[6]; m.p. 208–210°.

1-*Thiochromanone* (IX) *and* 1-*thiochromone* (X). These compounds were made from benzenethiol and β-chloropropionic acid by the methods of Arndt[9] and Krollpfeiffer,[10] m.p. 28° and 78° respectively.

1H-2,3-*Dihydro-naphtho*[2,1-b]*thiopyran*-1-*one* (XII) *and* 1H-*naphtho*[2,1-b]*thiopyran*-1-*one* (XIII). Compound XII was made from 2-naphthalenethiol and β-chloropropionic acid following the Krollpfeiffer procedure for IX,[10] m.p. 68–69°. This was dehydrogenated to the not previously reported 1H-naphtho[2,1-b]thiopyran-1-one by reaction with PCl_5 in benzene, following the procedure reported for the analogous dehydrogenation of 1-thiochromanone (see above); m.p. 116–117·5°. (Found: C, 73·3; H, 3·96; O, 7·67; S, 15·4. Calc. for $C_{13}H_8OS$: C, 73·6; H, 4·00; O, 7·54; S, 15·1%).

1H-*naphtho*[2,1-b]*pyran*-1-*one* (XIV). This compound was synthesized by the procedure described by Schmid and Seiler[11] for the preparation of the isomeric 4H-naphtho[1,2-b]pyran-4-one (XV). It was purified by sublimation (225–230°) followed by crystallization from pet. ether (m.p. 97·5–98·5°).

An attempt to prepare a thioketone from 1H-naphtho[2,1-b]pyran-1-one (XIII), by treatment with P_2S_5 in xylene or pyridine, failed.

We express our gratitude to Mr. R. Polain (Brussels) who recorded the NMR spectra.

The Belgian authors are indebted to the "*Fonds National de la Recherche Scientifique*" (*F.N.R.S.*) for a grant to purchase the spectrograph and to the "*Fonds de la Recherche Scientifique Fondamentale Collective*" for financial support.

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[7] *Organic Syntheses* (Edited by A. H. Blatt) Coll. Vol. II, p. 580 (1943).

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