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A STUDY BY ^{19}F NMR OF THE STRUCTURE OF 1,2-DITHIOLE DERIVATIVES AND CORRELATION WITH THE S_2p ELECTRON ENERGY DETERMINED BY *ESCA*

B. J. LINDBERG
Research Division, Pharmacia AB, 75125 Uppsala, Sweden

and

R. PINEL and Y. MOLLIER*
Laboratoire des Composés Thioorganiques Université de Caen, 14032 Caen Cedex, France

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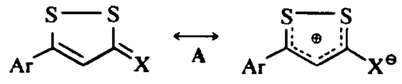
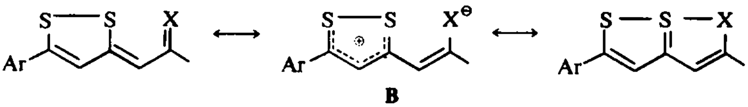
Abstract—A correlation is established between the ^{19}F NMR chemical shifts and the S_2p electron energies measured by ESCA in the 1,2-dithiole derivatives. This correlation shows that the fluorine chemical shifts depends on the positive charge taken by the 1,2-dithiole ring and then constitutes a convenient evaluation of this charge.

It is known that the position of the NMR signal of ^{19}F in the *p*-substituted fluorobenzenes is particularly sensitive to the inductive and mesomeric effects of the substituent. We can thus connect the chemical shift of the fluorine with the effect of the *para* substituent on the phenyl σ and π electrons.[1] This method has been used recently for cyclopropenone derivatives[2,3] in order to examine the importance of the contribution to the resonance of a mesoionic limit form.

In our various studies[4,8] on 1,2-dithiole derivatives, we have also discussed the contribution of mesoionic form in the description of compounds of type A, B, C.





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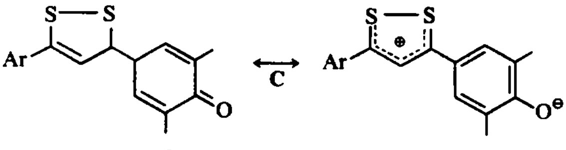


X = O or S   Ar = phenyl or *p*-fluorophenyl

In these compounds, the carbon 5 of the 1,2-dithiole ring has an electron density less than unity.[8,14] Thus in all cases where Ar = *p*-fluorophenyl, the 1,2-dithiole ring exerts a large negative mesomeric effect on the fluorobenzene; i.e. it tends to induce a positive charge on the carbon in the *para* position. The observed chemical shift in NMR of the fluorine constitutes, in a way, a measure of the electron-attracting effect of the 1,2-dithiole ring on the π electrons of the *p*-fluorophenyl substituent. Thus an increase of the positive charge on the 1,2-dithiole ring will cause a down field shift of the signal of ^{19}F.

The importance of the positive charge taken by the 1,2-dithiole ring may be estimated by other methods. Particularly calculations by various methods[9-11] show an important variation of charge density on the S atoms which thus accounts for the more or less positive character of this heterocycle. Furthermore we have also studied these compounds by ESCA[15] and have determined the S_2p electron binding energy. This energy depends on the distribution of the valence electrons around the considered atom, i.e. of the total charge on this atom. Thus the shift of the S_2p electron binding energies of the 1,2-dithiole ring relative to that of the sulphur molecule (164·2 eV), constitutes a measure of the charge on the S atoms, and its variation reflects the variation of the positive charge taken by this heterocycle. Consequently, one could expect a correlation between these energies and the chemical shift of ^{19}F. In the Table we have gathered the results obtained from two series of 1,2-dithiole derivatives, where Ar = phenyl and *p*-fluorophenyl.

Although the S_2p electron binding energy range is small, a plot of the ^{19}F chemical shifts versus the S_2p electron binding energies for the 1,2-dithiole ring shows that there may be a linear correlation between these two types of measures, Fig 1 (bold line, correlation coefficient = 0·96). This correlation thus suggests that the chemical shift of ^{19}F reflects the variation of the positive charge taken by the 1,2-dithiole ring and thus allows to obtain an idea of the importance of this charge.

A comparison of the S_2p electron binding energies of the two series of 1,2-dithiole compounds shows that the fluorine substituent does not cause any significant shifts of these energies. The differences do not in any case exceed the experimental error limits (±0·2 eV). A plot of the ^{19}F chemical shifts of the flourine substituted series versus the S_2p electron binding energies of the unsubstituted series gives a regression line of approximately similar slope as in the substituted series (correlation coefficient 0·91) and slightly displaced (0·1 eV) in the positive direction of the S_2p electron binding energy axis (dashed line in Fig 1). Considering the error limits, this displacement is hardly statistically significant. This means that the +M and −I substituent effects of *para* fluorine on the 1,2-dithiole ring practically balance each other (or, if the displacement be real very nearly balance each other with a small possible predominance of the +M effect).

Aromatic substituent effects on ESCA shifts have previously been shown to be a second order effect[15,16] and the present result shows in particular that the effect of *para* fluorine is very small. We are thus justified to correlate ^{19}F NMR shifts in *p*-substituted fluorobenzenes with the ESCA shifts of the substituents, even if these have not been measured in the same series.

Treating a series of sulphur-substituted aromatic *p*-fluoro compounds in this manner[18] the correlation shown in Fig 2 was obtained (correlation coefficient = 0·98). In this case average sulphur shifts from the aromatic groups were taken from a previous investigation[16] including aromatic sulphur compounds with various substituents. The ^{19}F shifts were taken from Ref 19. The result is again a rectilinear correlation over a much larger range of S_2p electron binding energies and with a slope of the same sign as in Fig 1.

The binding energies of F_1s electrons (ESCA) in compounds **2b** to **8b** are 687·4 ± 0·2 eV. Considering the experimental error they are nearly constant. This result shows that the electronic density on the fluorine atom varies very little with the nature of the 1,2-dithiole derivative. This fact is in agreement

Table 1. δ ^{19}F NMR and S_2p electron binding energies (ESCA) for the 1,2-dithiole derivatives

Compound	Ar = C_6H_5 **a** Ar = *p*-F-C_6H_4 **b**	ESCA $E_{S_{2p}}$ (eV) Ar = phenyl	ESCA $E_{S_{2p}}$ (eV) Ar = *p*-F-C_6H_4	δ ^{19}F (ppm) internal Ref $CFCl_3$, solvent: DMSO Ar = *p*-fluorophenyl
3-Aryl-1,2-dithiolylium perchlorate	**1a,b**	165·2	164·9	102·42
3-Methylthio-5-*p*-fluorophenyl-1,2-dithiolylium iodide	**2b**		165	103·02
5-Aryl-1,2-dithiole-3-thione (type A)	**3a**	164·5		106·99
5-Aryl-1,2-dithiole-3-one (type A)	**4a,b**	164·7	164·4	107·49
2,6-Dimethyl-4-(5-aryl-1,2-dithiole-3-ylidene) cyclohexadienone (type C)	**5a,b**	164·6	164·4	107·83
2-(5-Aryl-1,2-dithiole-3-ylio) phenolate (type B)	**6a**	164·2		107·80
(5-Aryl-1,2-dithiole-3-ylidene) acetophenone (type B)	**7a,b**	164·0	164·2	109·05
2-(5-Aryl-1,2-dithiole-3-ylidene) cyclohexanone (type B)	**8a,b**	163·9	163·9	109·57

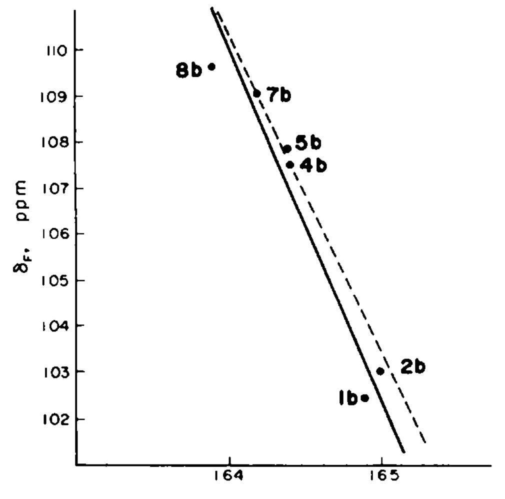


Fig 1. ^{19}F NMR shift (internal Ref $CFCl_3$) in 1,2-dithiole derivatives ($Ar = p\text{-}F\text{-}C_6H_4$) versus S_2p electron binding energy (bold line).

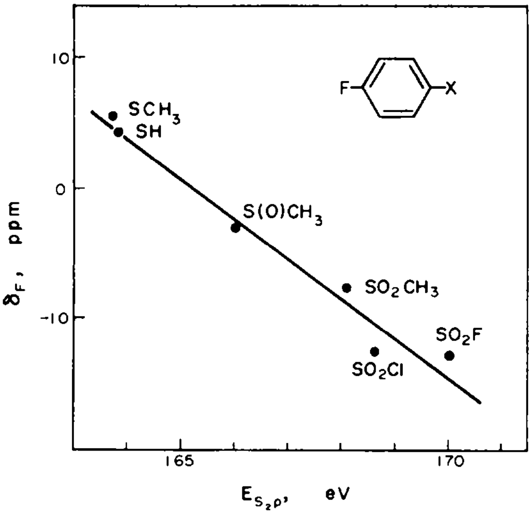


Fig 2. ^{19}F NMR shift (internal Ref C_6H_5F) in sulfur *para*-substituted fluorobenzenes versus S_2p electron binding energy[18].

with previous studies[17] showing that the charge ($\sigma + \pi$) variation on the fluorine is very small when one considers fluorobenzenes *para* substituted by various groups with acceptor mesomeric effect. Comparing this result with the small effect of fluorine substitution on the S_2p electron binding energies, it is very satisfying to find that the effects on the ESCA shifts are the same at both ends of the conjugated system.

It has been shown theoretically and experimentally that one cannot expect a general correlation between NMR and ESCA shifts[20], particularly when considering the same atom in widely varying molecular environments. A substituted aromatic series presents a different situation. The nearest environment of an invariant substituent on *p*-fluorine in the present investigation remains the same, provided that there are no important intermolecular forces. We therefore believe that the observations made in this paper indicate, that in special cases, there may exist good correlations between NMR and ESCA shifts, which could be of value in the investigation of substituent effects. We suggest that the possible use of ESCA shifts as a measure of substituent effects should be systematically and thoroughly investigated.

Physical methods

The ESCA spectra of compounds **1a** to **8a** were previously published[15].

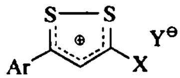
The ESCA spectra of compounds **1b**, **2b**, **4b**, **5b**, **7b** and **8b** were determined at IRCHA (Vert-le-Petit—France) in a Varian IEE spectrometer; the samples were mounted on a piece of double-sided Scotch Tape. The indicated S_2p and F_1s energies are corrected values referred to the carbon peak at 285·0 eV, according to the previously used calibration method.[15,22]

The NMR spectra of ^{19}F have been determined on a Brucker apparatus at 84·66 Mhz, in dimethylsulfoxide as a solvent. The concentrations used are about 0·2 mole/l. The chemical shifts given in ppm are referred to trichlorofluoromethane used as an internal reference. We checked that large variations of concentration introduced an error always less than ±0·3 ppm. Errors due to incertainties in the concentration are thus negligible with regard to the chemical shift variations of ^{19}F for the various compounds studied.

EXPERIMENTAL

Preparation of compounds

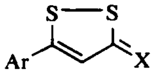
Most compounds studied in this paper were prepared according to published methods. References and m. ps are given in the following list:



Compound **1a** 3-phenyl-1,2-dithiolylium perchlorate $X = H$, $Y = ClO_4$, F = 180–182°5.[21]

Compound **1b** 3-*p*-fluorophenyl-1,2-dithiolylium perchlorate was prepared according to Klingsberg.[21] $X = H$, $Y = ClO_4$, F = 145°. $C_9H_6FClO_4S_2$: (Found: C, 36·49 H, 2·05 Calc for C, 36·63 H, 2·04%)

Compound **2b** 3-methylthio-5-*p*-fluorophenyl-1,2-dithiolylium iodide. $X = SCH_3$, $Y = I$, F = 170°. Prepared according to Ref 28. $C_{10}H_8FIS_3$: (Found: C, 32·45 H, 2·05 Calc for C, 32·43 H, 2·17%)

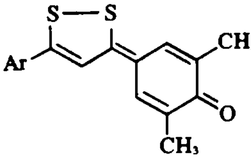


Compound **3a** 5-phenyl-1,2-dithiole-3-thione. $X = S$, F = 126°.[24]

Compound **3b** 5-*p*-fluorophenyl-1,2-dithiole-3-thione. $X = S$, F = 116°.[23]

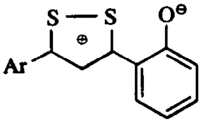
Compound **4a** 5-phenyl-1,2-dithiole-3-one. X = O, F = 117°.[21]

5-*p*-Fluorophenyl-1,2-dithiole-3-one (**4b**), X = O, F = 82°. The 5 - *p* - fluorophenyl - 1,2 - dithiole - 3 - thione (0·1 m) was dissolved in chloroform on a water bath. A soln of mercuric acetate (0·02 m) in AcOH was added and the mixture was refluxed *ca* ¼ h. The ppt was filtered and the filtrate was treated like in Ref 25. $C_9H_5FOS_2$: (Found: C, 50·95; H, 2·40 Calc for C, 50·91; H, 2·37%).



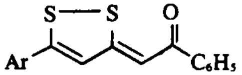
Compound **5a** 2,6 - dimethyl - 4 - (5 - phenyl - 1,2 - dithiole - 3 - ylidene) cyclohexadienone, F = 218°.[23]

Compound **5b** 2,6 - dimethyl - 4 - (5 - *p* - fluorophenyl - 1,2 - dithiole - 3 - ylidene) cyclohexadienone, F = 211°.[23]



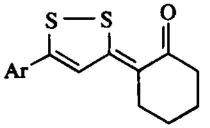
Compound **6a** 2 - (5 - phenyl - 1,2 - dithiole - 3 - ylio) phenolate, F = 157°.[5]

Compound **6b** 2 - (5 - *p* - fluorophenyl - 1,2-dithiole - 3 - ylio) phenolate. Prepared according to Ref 5. F = 178° $C_{15}H_{10}FOS_2$: (Found: C, 62·72; H, 3·24. Calc for C, 62·47; H, 3·15%).



Compound **7a** (5 - phenyl - 1,2 - dithiole - 3 - ylidene) acetophenone, F = 135°.[26]

Compound **7b** (5 - *p* - fluorophenyl - 1,2 - dithiole - 3 - ylidene) acetophenone, F = 206°.[27]



Compound **8a** 2 - (5 - phenyl - 1,2 - dithiole - 3 - ylidene) cyclohexanone, F = 140°.[5,7]

Compound **8b** 2 - (5 - *p* - fluorophenyl - 1,2 - dithiole - 3 - ylidene) cyclohexanone. Prepared according to.[5] F = 134° $C_{15}H_{13}FOS_2$: (Found: C, 61·78; H, 4·45. Calc for C, 61·61; H, 4·48%).

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