

Substituent Effects of Sulfur Groups

III. The Influence of Conjugation on ESCA Spectra of Sulfur Substituted Nitrobenzenes

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The chemical shifts in the ESCA spectra of a series of sulfur substituted nitrobenzenes have been analysed and compared with shifts in other aromatic sulfur compounds. The shifts are discussed in terms of resonance between simple canonical structures, and a small influence of the +M effect of bivalent sulfur on the position of the electron lines is observed. The effect is enhanced by a specific proximity interaction with bivalent sulfur groups in the *ortho* position.

In a previous investigation on the ESCA shifts of sulfur groups it was found that the electron binding energy of the sulfur atom of the group is characteristic of the group.¹ These "group shifts" are of great interest for the identification of groups or structural elements in molecules in the analysis of chemical structure. The usefulness of group shifts in general structural analysis is dependent on their constancy. The group shifts of groups linked both to aliphatic carbon and variously substituted aromatic systems vary little with the structure of the rest of the molecule, *i.e.* the first order effect on the shifts is mainly determined by the nature of the nearest atom to which the group is linked. Substituent effects are thus only of second order importance from the general functional group analysis point of view. However, for a refined and more sophisticated analysis and especially from the theoretical point of view it is desirable to gain some understanding of small second order effects on ESCA shifts. In the present investigation we have tried to approach this problem by undertaking a detailed systematic study of previously recorded ESCA spectra of a series of sulfur substituted nitrobenzenes, covering a large range of substituents with sulfur in different oxidation states.

In the discussion of small effects, it is of course important that the measuring technique is accurate, and that the influence of solid state effects, molecular potentials¹ a.s.o. does not vary. Our experience with the ESCA technique has now come to a stage where we think that the first requirement can be fairly well satisfied, and by choosing a large structurally uniform series of molecules, which are not too small compared with the groups studied, we have attempted to meet the second requirement.

Since the nitro group is a strong $-M$ substituent, electron donating conjugation from this group is absent. Sulfur groups in an oxidation state with only one lone electron pair, which has predominantly s character, do not show any great tendency to $+M$ conjugation with $-M$ groups.² In the case of the

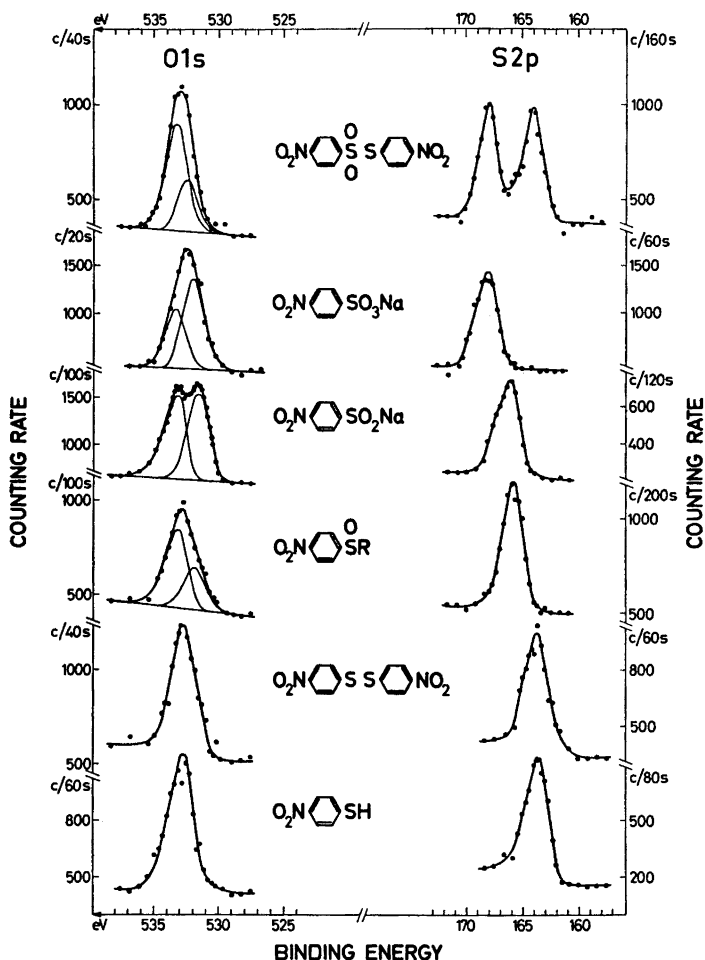
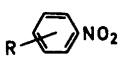


Fig. 1. $O1s$ and $S2p$ electron lines from some *para* sulfur substituted nitrobenzenes. For the sulfoxide $R=CH_3$, for the $O1s$ spectrum and $R=p-C_6H_4NO_2$ for the $S2p$ line.

Table 1. S2p, N1s, and O1s electron binding energy shifts of sulfur and the nitro group in sulfur substituted nitrobenzenes. Reference values; S2p 163.4 eV, N1s 405.8 eV, and O1s 533.0 eV.

		<i>q</i>	S2p	N1s	O1s
-H				0	0
-SK	<i>m</i> -	-0.51	-2.1		0.1
-SNa	<i>p</i> -	-0.47	-2.2	0.0	0.2
-SH	<i>o</i> -	-0.04	0.7	0.1	0.0
	<i>p</i> -	-0.04	0.3	-0.1	-0.2
-SCH ₃	<i>o</i> -	0.00	0.5		
	<i>p</i> -	0.00	0.3		
-SC ₆ H ₄ CH ₃	<i>o</i> -	0.00	0.6	0.1	0.0
	<i>p</i> '-	0.00	0.2	0.0	-0.1
-SC ₆ H ₄ NO ₂	<i>o</i> -	0.00	0.8	0.2	0.0
	<i>o</i> '-	0.00	0.3	0.0	0.2
-SSC ₆ H ₄ NO ₂	<i>p</i> -	0.00	0.7	0.0	0.1
	<i>o</i> -	0.00	0.7	-0.1	0.1
	<i>m</i> -	0.00	0.4	-0.1	-0.1
	<i>p</i> '-	0.00	0.3	-0.2	-0.3
-SSO ₂ C ₆ H ₄ NO ₂	<i>p</i> -	0.00	0.6	0.0	0.2
-SNH ₂	<i>o</i> -	0.06	0.9	0.4	0.2
-SCl	<i>o</i> -	0.06	0.7	0.2	0.0
-SOCH ₃	<i>o</i> -	0.22	1.8	0.1	0.2
-S(O)CH ₃	<i>o</i> -	0.44	2.6	0.5	0.4
	<i>m</i> -	0.44	2.6		0.1
	<i>p</i> -	0.44	2.5	0.3	0.1
-S(O)C ₆ H ₄ NO ₂	<i>o</i> -	0.44	2.8	0.0	
	<i>o</i> '-	0.44	2.7	0.1	
-SO ₂ Na	<i>o</i> -	0.56	2.6		0.3
	<i>m</i> -	0.56	2.5		0.3
	<i>p</i> -	0.56	2.6	0.3	0.4
-SOOCH ₃	<i>o</i> -	0.66	4.0	0.1	0.1
	<i>m</i> -	0.66	3.8	-0.1	-0.1
	<i>p</i> -	0.66	4.1	0.0	0.3
-SO ₂ CH ₃	<i>o</i> -	0.88	4.7		
	<i>m</i> -	0.88	4.6	0.0	0.1
	<i>p</i> -	0.88	4.8	0.5	
-SO ₂ C ₆ H ₅	<i>p</i> -	0.88	4.4	0.2	0.2
-SO ₂ C ₆ H ₄ NO ₂	<i>p</i> '-	0.88	4.5	0.0	0.2
-SO ₂ SC ₆ H ₄ NO ₂	<i>p</i> -	0.88	4.8	0.0	0.2
	<i>p</i> '-	0.88	4.8	0.0	0.2
-SO ₂ NH ₂	<i>m</i> -	0.94	5.0	0.1	0.1
-SO ₂ Cl	<i>o</i> -	0.94	5.3	0.3	0.6
	<i>m</i> -	0.94	5.1	-0.2	0.0
	<i>p</i> -	0.94	5.1	0.6	0.6
-SO ₂ Na	<i>o</i> -	1.00	4.9	0.2	-0.3
	<i>m</i> -	1.00	4.9	0.0	-0.5
	<i>p</i> -	1.00	4.8	0.4	0.1
-SO ₂ OCH ₃	<i>o</i> -	1.10	5.1	0.1	0.3
	<i>m</i> -	1.10	5.0	0.0	0.1
	<i>p</i> -	1.10	5.0	0.1	0.2
-SO ₂ F	<i>o</i> -	1.31	6.4	0.1	0.6
	<i>p</i> -	1.31	6.8		

sulfinate group detailed investigations have proved the absence of a +M conjugation of the sulfinate group with the -M nitro group.^{3,4} It can thus only be expected that the bivalent sulfur groups with a lone *p* electron pair could show a +M conjugation with the nitro group.

During the course of our ESCA investigations on substituent effects, it has been found that with a large body of data, small systematic trends in the substituent effects due to conjugation can be distinguished. In order to provide some background to the significance of such trends, we shall first discuss the results from the point of view of general substituent effects and then proceed to analyse the possible effect of +M sulfur groups on the ESCA spectra of sulfur, oxygen, and nitrogen in a series of sulfur substituted nitrobenzenes.

The discussion is based on experimental results from a previous paper¹ and the relevant data for the sulfur substituted nitro compounds are collected in Table 1, in which the S2*p*, O1*s*, and N1*s* electron binding energy shifts are given. Some examples of electron spectra are given in Fig. 1.

CORRELATION WITH CHARGE

In previous electron spectroscopic investigations⁵⁻⁷ it has been shown that the ESCA shifts correlate very well with the charge on an atom in a molecule estimated by using the concept of partial ionic character of bonds as a function of the electronegativity difference between the atoms forming the bonds.

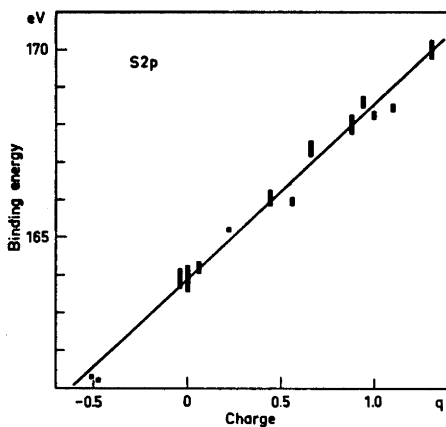


Fig. 2. Correlation between S2*p* binding energies in sulfur substituted nitrobenzenes and charge.

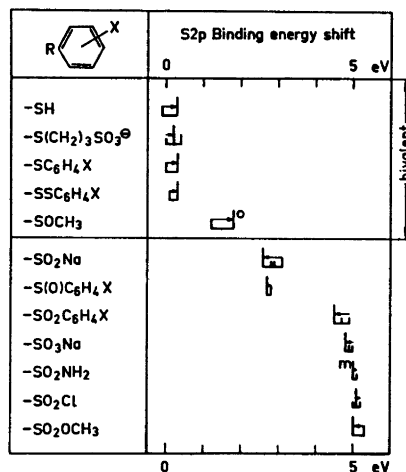


Fig. 3. S2*p* electron binding energy shifts in substituted aromatic sulfur compounds. Long vertical line: X=*p*-nitro (except when superscript indicates otherwise). Medium vertical line: =unsubstituted. Short vertical line: X=other substituents (see Table 2).

This treatment is now well established for sulfur and that it holds good also for the present series of compounds is shown by Fig. 2, in which the S2*p* binding energies for the sulfur groups are plotted against the charge parameter. We shall therefore apply the concept of a consistent charge-shift relationship to the discussion of the results, and for the details of the calculations the reader is referred to Ref. 5.

GENERAL INFLUENCE OF AROMATIC SUBSTITUENT EFFECTS*

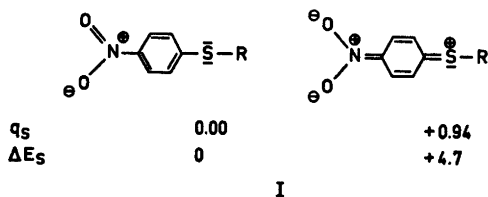
For comparison of the S2*p* binding energies of nitro substituted compounds with those of corresponding unsubstituted sulfur compounds or sulfur compounds with less electron withdrawing substituents than the nitro group data from Ref. 1 have been collected in Table 2. In Fig. 3 comparison has been made with the *para* nitro substituted compounds except in cases where the *para* compounds were not available.

Table 2. S2*p* electron binding energy shifts in aromatic sulfur compounds with other substituents than the nitro group. Reference value 163.4 eV.

Compound	S2 <i>p</i>	Compound	S2 <i>p</i>
PhSH	-0.1	<i>p</i> -(<i>p</i> -H ₃ CC ₆ H ₄ SO ₂)C ₆ H ₄ N	4.9
PhS(CH ₂) ₃ SO ₃ Na	0.4	<i>p</i> -(<i>p</i> -H ₃ CC ₆ H ₄ SO ₂)C ₆ H ₄ NO	
<i>o</i> -NH ₂	0.0	PhSO ₂ Ph	
<i>p</i> -Cl	0.0	<i>p</i> , <i>p</i> '-NH ₂	4.7
<i>p</i> -NO ₂	0.2	PhSO ₂ Na	
PhSPh	0	<i>p</i> -N(CH ₃) ₂	4.9
PhSSPh	0.8	<i>p</i> -NH ₂	4.9
bis <i>p</i> -N(CH ₃) ₂	0.1	<i>m</i> -CO ₂ Na	5.0
PhSOCH ₃	1.2	<i>p</i> -CO ₂ Na	5.0
<i>p</i> -Cl	1.2	PhSO ₂ NH ₂	
PhS(O)Ph	2.8	<i>p</i> -NH ₂	5.1
PhSO ₂ Na	3.1	PhSO ₂ Cl	
<i>m</i> -CO ₂ Na	2.8	<i>p</i> -CH ₃	5.2
<i>p</i> -CO ₂ Na	2.9	3-Cl, 4-NH ₂ , 5-SO ₂ Cl	5.0
<i>p</i> -Cl	3.1	PhSO ₂ OCH ₃	5.3

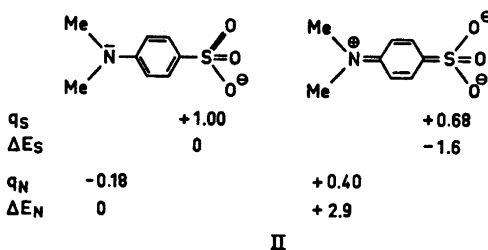
The electron withdrawing effect of the nitro group would make the sulfur in the sulfur groups more positive. Hence the nitro group would be expected to cause a positive shift in the binding energy of the sulfur groups. With sulfur groups of higher valency than bivalent this is in no case observed. On the contrary negative shifts are seen in several cases. This indicates that the influence of solid state effects and other second order effects overshadow the influence of a -I substituent effect of the nitro group on the sulfur shifts. Only with bivalent *para* sulfur groups are shifts in the expected direction observed, which suggests a small influence of their +M effect on the 2S*p* shifts. However, these shifts do not exceed the order of magnitude of the

shift range of the general second order effects, which for the groups of higher valency than bivalent do not exceed ~ 0.5 eV. A charge calculation (I) based on the treatment described in Refs. 5 and 6, shows that one should expect a shift of 4.7 eV for 100 % contribution of the conjugated structure. Hence a contribution of more than 10 % of the conjugated structure to the resonance hybrid is required in order to shift the binding energies of groups significantly outside the general range of group shifts. Only with very strong $-M + M$ conjugation have significant shifts outside the general group shift range been observed (see below).



As has been discussed in a previous paper of this series,⁸ sulfur groups of a higher oxidation state are $-M$ groups. One could therefore expect electron accepting conjugation with $+M$ substituents for these groups. This case is here represented by the *para* dimethylamino and *para* amino sulfonate. The sulfonate group has previously been shown to conjugate,⁸⁻¹⁰ but the conjugation is weakened by its charge,^{8,10} In Fig. 3 there is no evidence of any influence of this conjugation on any of the sulfur shifts.

A charge calculation shows in this case that the influence of conjugation on the sulfur could be expected to be less than in the case of bivalent sulfur (II). The sulfur atom will mainly function as a relay for the electron displacement, and hence the absence of significant shifts is in accord with what could be expected from this calculation. Calculations of this type show that signi-



ficant effects of conjugation on ESCA spectra will be more likely for the terminal atoms in the conjugated system. According to the calculation the influence of the conjugation on the nitrogen would be expected to be somewhat larger than on the sulfur. In Table 3 available data on the amino nitrogen has been collected and compared. No significant shifts in a positive direction can be observed in the compounds with *para* sulfur groups except for the

Table 3. N1s electron binding energies for conjugated amino groups in sulfur substituted aromatic compounds.

Compound	N1s	Δ N1s	Ref.
$\text{H}_2\text{NC}_6\text{H}_5$	399.6	0	6 ^a
<i>p</i> - $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$	399.1	-0.5	6 ^a
<i>p,p'</i> - $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$	399.4	-0.2	1
<i>p</i> - $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NH}_2$	400.0	+0.4	6 ^a
<i>p,p'</i> -(H_3C) ₂ NC ₆ H ₄ SSC ₆ H ₄ N(CH ₃) ₂	399.7	0	1
<i>p</i> -(H_3C) ₂ NC ₆ H ₄ SO ₃ Na	399.3	-0.4	6 ^a

^a Calibration revised.

para aminobenzenesulfonamide, in which the sulfur group could be expected to be the strongest -M group. This shift is, however, within the limit of the general second order effects, and the result leads to the conclusion that the -M effect of sulfur groups on ESCA shifts is negligible.

The general impression is thus that both inductive and mesomeric aromatic substituent effects in sulfur groups have only a small influence on the ESCA shifts of sulfur. The shifts can therefore be used with confidence for the identification of groups in the general analysis of functional groups in aromatic compounds. If aromatic substituent effects are to be studied by means of ESCA, one must therefore adopt special measures in order to separate them from general second order effects.

SUBSTITUENT EFFECTS IN THE NITROBENZENE SERIES

Sulfur shifts. In Fig. 4 the shifts for sulfur in the *o*-, *m*-, and *p*-sulfur substituted nitrobenzenes are presented. The shifts for the groups of higher valency show a very consistent picture, with a shift range in all cases within the experimental error limits. This fact seems to indicate, that the second order effects, like solid state effects, influence of crystal potentials a.s.o., do not vary significantly in this series. Further there is no significant difference between the *o*-, *m*-, and *p*-shifts in the groups of higher valency. In the light of this fact the rather large shifts observed between the *o*- and *p*-groups in the bivalent substituents are striking. In all these groups there is a significant *ortho-para* shift of about 0.4 eV.

Unfortunately too few *meta* compounds were available for a systematic comparison between *meta* and *para* shifts for bivalent sulfur groups.

Ortho effects due to an interaction between nitro group oxygen and sulfur (III) in the reactions of sulfenyl derivatives have recently been demonstrated.¹¹ An X-ray crystallographic analysis of *ortho* nitrobenzene sulfenate ester has revealed an abnormally short distance between the sulfur and the oxygen of the nitro group,¹² and this finding was explained as a strong "nonbonding" interaction between sulfur and oxygen. The effect of such an interaction on

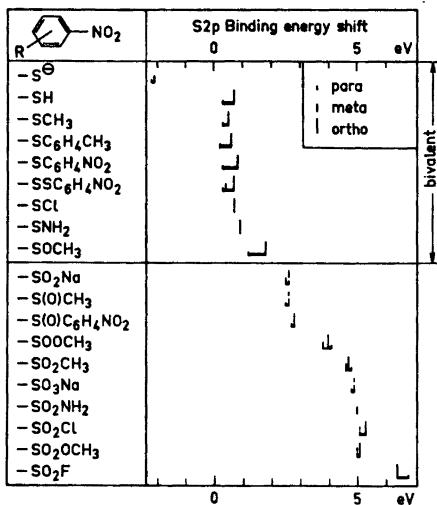


Fig. 4. S2p electron binding energy shifts in sulfur substituted nitrobenzenes.

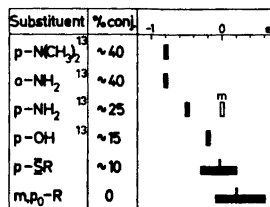
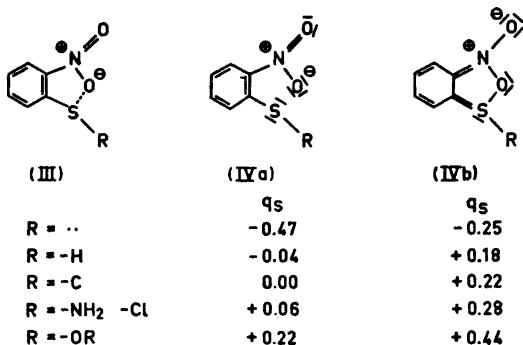


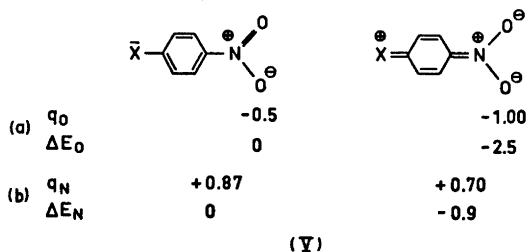
Fig. 5. O1s electron binding energy shifts of the nitro group in nitrobenzenes substituted with +M groups.

the ESCA shifts of sulfur can be qualitatively estimated by a calculation using the canonical structures IV. A contribution of structure IVb to the resonance hybrid would cause a positive sulfur shift. In the sulfenate group the sulfur is made more positive by the oxygen and this could be expected to assist the interaction with the negative oxygen of the nitro group. Unfortunately, the *para* nitro sulfenyl compounds were not stable. The *ortho* shift of the sulfenate ester has therefore been compared with the shift of the *para* chlorobenzenesulfenate¹ in Fig. 4, and this *para-ortho* shift appears rather large.

Oxygen shifts. We have now seen that there is a weak influence of +M conjugation of bivalent sulfur on the S2p sulfur shifts. The charge calculation on the nitro group leads to the expectation that the oxygen in this group



would be sensitive to +M effects (V). This expectation is substantiated by Fig. 5 in which the O1s binding energies for the nitro group in nitrobenzenes substituted with strong +M *para* or *ortho* groups are represented. The $p\text{-}\bar{S}\bar{R}$ symbol represents the shift interval covered by all the bivalent *para* sulfur groups from Table 1. The $m,p_o\text{-R}$ symbol represents the shift interval covered by the remaining nitro substituents. It is obvious that the bivalent sulfur groups show a much smaller +M effect than the typical strong +M groups, and it is near the limit of significance. In Fig. 5 the degree of conjugation interpolated from the calculation on the canonical structures represented in (Va) are also shown. It is interesting to observe, that the value for the average



of the bivalent sulfur groups is in good agreement with what should be expected from I, which also leads to about 10 % conjugation. Thus the sulfur and oxygen shifts together seem to indicate that a small +M effect is present in the bivalent sulfur groups. One should then also expect that the difference

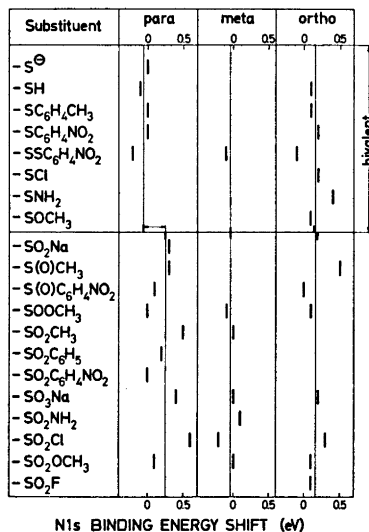
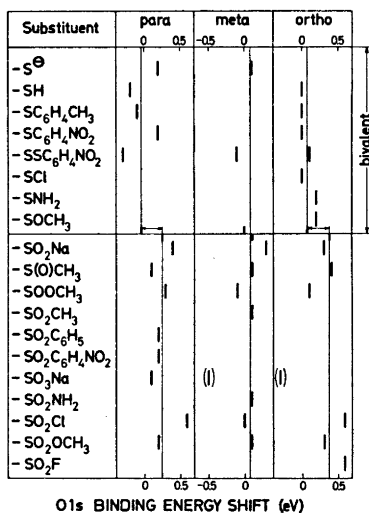


Fig. 6. O1s electron binding energy shifts of the nitro group in sulfur substituted nitrobenzenes.

Fig. 7. N1s electron binding energy shifts of the nitro group in sulfur substituted nitrobenzenes.

between the O1s shifts of the nitro group with the bivalent *para* sulfur substituents should be more negative than those with *para* sulfur groups of higher valency. Further one should expect a smaller difference between bivalent and higher valent groups for the *meta* substituted compounds. The representation of the oxygen shifts given in Fig. 6 seems to suggest that this is actually the case. However, the effect is small, and being near to the error limits, it could never have been observed by a comparison of only a few compounds. Hence the study of conjugative effects by means of ESCA requires systematic studies of compounds with large series of substituents.

The result from this comparison is consistent with a small +M conjugation of the bivalent sulfur groups with the -M nitro group, with an order of magnitude near the limit of detectability. The smallness of this effect adds more significance to the specific *ortho* effect discussed in the preceding paragraph.

Nitrogen shifts. The charge calculation on nitrogen in substituted nitrobenzenes leads to the expectation that nitrogen essentially only would relay the mesomeric effects (Vb). The nitrogen shifts from Table 1 have been collected in Fig. 7. With a +M effect from the *para* sulfur groups, one should according to the calculations expect a slight N1s shift in a negative direction in the nitro groups with bivalent *para* sulfur substituents when compared with *para* sulfur substituents of higher valency. Fig. 7 suggests a presence of such a shift. Thus the same effect as seen in the sulfur and oxygen shifts shows up also in the nitrogen shifts. On the basis of the charge calculation the susceptibility of the nitrogen to conjugation effects seems relatively greater than that of sulfur groups of higher valency (II). Again, considering the error limits, this shift must be considered small, and could not have been detected using only a few compounds.

CONCLUSION

The ESCA shifts of sulfur, oxygen and nitrogen in sulfur substituted nitrobenzenes are influenced by the substituent effects in a remarkably consistent manner. The substituent effects on all three elements suggest the presence of a small -M - +M conjugation of the nitro group with the bivalent sulfur groups.

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