Substituent Effects of Sulfur Groups

IV. Correlation of Polarographic Half-wave Potentials and Asymmetric NO Stretching Vibrations with ESCA Shifts in Sulfur Substituted Nitrobenzenes

BERNT J. LINDBERG

Research Division, Pharmacia AB, Uppsala, Sweden

BARBRO SCHRÖDER

Chemical Institute, University of Uppsala, Uppsala, Sweden

The NO stretching vibrations for the nitro group in a series of sulfur substituted nitrobenzenes have been measured. The wave numbers as well as previously measured polarographic half-wave potentials have been correlated with ESCA shifts ($S2p$ electron binding energies) for the sulfur substituents. The results indicate that the binding energies of the sulfur atom linking the sulfur groups to the aromatic ring reflect the inductive substituent effects of these groups.

Since some examples of good correlations of asymmetric NO stretching vibrations in substituted nitrobenzenes with substituent constants have appeared in the literature, an IR spectroscopic investigation of sulfur substituted nitrobenzenes was initiated with the intention to utilize the asymmetric NO vibration for the estimation of Hammett substituent constants for certain sulfur groups. However, the Hammett plots obtained with an increased number of substituents were not good enough for the original purpose. In the meantime additional physico-chemical data became available for the sulfur substituted nitrobenzenes from polarographic [1] and electron spectroscopic [2a] (ESCA) investigations, in which half-wave potentials for the nitro group and ESCA shifts for sulfur, oxygen, and nitrogen were determined.

It was found to be of interest to interrelate all three of these physico-chemical parameters, and in this paper we have made an attempt to gain a better understanding of aromatic substituent effects, by cross-correlating the data in various ways and in such a manner that information is obtained

which could not have been gained by considering each parameter alone. In this way an additional dimension was introduced in the "correlation" chemistry, which proved useful in the elucidation of the importance of ESCA shifts in physical organic chemistry.

ELECTRON SPECTROSCOPY

In the previous investigation of this series the S2p electron binding energies for sulfur in sulfur substituted nitrobenzenes measured by the ESCA technique were discussed from the point of view of aromatic substituent effects.[2a,b] It was found that the substituent effects on the sulfur groups were rather small, and with the present error limits of the technique they are too small to be useful in the general study of substituent effects using only one single sulfur group as the object of study.

In the present investigation, the problem was therefore reversed to deal with the question of whether the substituent effects of various sulfur groups on the properties of another invariant group show any useful correlation with electron binding energies of sulfur. For this purpose the S2p electron binding energy of the sulfur atoms linking the sulfur groups to the aromatic ring in the

Table 1. S2p electron binding energies (E_b) and polarographic half-wave potentials ($E_{\frac{1}{2}}$) for a series of sulfur substituted nitrobenzenes.

Substituent	E_b eV	$E_{\frac{1}{2}}$ $-mV$		
		pH 5.0	pH 7.2	pH 9.3
m-S$^\ominus$/SH	161.3/164.0	375	485	570
p-S$^\ominus$/SH	161.2/163.7	403	518	637
o-SCH$_3$	163.9	393	540	620
m-SCH$_3$	164.0	370	500	587
p-SCH$_3$	163.7	406	537	635
o-S(O)CH$_3$	166.0	287	463	518
m-S(O)CH$_3$	166.0	332	468	566
p-S(O)CH$_3$	165.9	338	474	550
o-SO$_2$CH$_3$	168.1	347	461	508
m-SO$_2$CH$_3$	168.0	326	479	556
p-SO$_2$CH$_3$	168.2	269	408	509
m-SO$_2$NH$_2$	168.4	346	492	599
p-SO$_2$F	170.2	232	341	—
o-SOO$^\ominus$	166.0	407	594	743
m-SOO$^\ominus$	165.9	380	563	671
p-SOO$^\ominus$	166.0	363	553	650
o-SOOCH$_3$	167.4	273	408	538
m-SOOCH$_3$	167.2	310	462	552
p-SOOCH$_3$	167.5	287	421	502
o-SO$_3$$^\ominus$	168.3	555	697	778
m-SO$_3$$^\ominus$	168.3	447	606	686
p-SO$_3$$^\ominus$	168.2	414	598	651
o-SO$_2$OCH$_3$	168.5	330	473	541
m-SO$_2$OCH$_3$	168.4	302	452	545
p-SO$_2$OCH$_3$	168.4	257	390	481

series of sulfur substituted nitrobenzenes was utilized as a correlation parameter in studying the substituent effects of the sulfur groups on the polarographic half-wave potentials and the asymmetric NO vibrations of the nitro group.

The ESCA data, taken from Ref. 2a, as well as the sulfur groups used, are given in Tables 1 and 3, and the correlations are presented and discussed in the following paragraphs.

POLAROGRAPHY

In the investigation of the substituent effects of the sulfur groups on the half-wave potentials of the nitro group, described in Ref. 1, a good correlation with Hammett constants was found for all substituents which are reduced by an identical mechanism, and the σ_p^- constants apply for *para* −M groups. Charged substituents and a few others deviate from the common mechanism and do not fit the Hammett equation. In the present investigation this knowledge has been utilized for further correlations, and the relevant data are collected in Table 1.

Correlation with S2p electron binding energies. In Fig. 1 the polarographic half-wave potentials for the aromatic nitro group have been plotted against
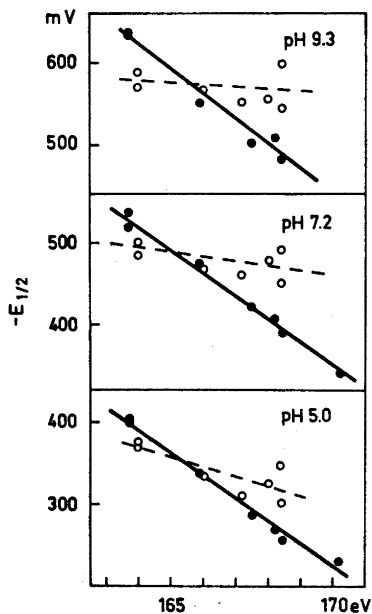

Fig. 1. Correlation of polarographic half-wave potentials $(E_{\frac{1}{2}})$ for the nitro group with S2p electron binding energies (E_b) for neutral *para* and *meta* sulfur groups in substituted nitrobenzenes; O *meta*, ● *para*.
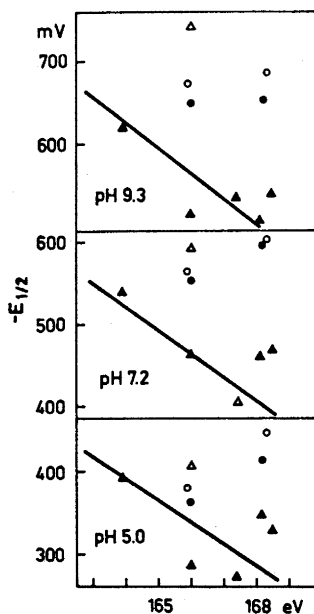
Fig. 2. Correlation of polarographic half-wave potentials $(E_{\frac{1}{2}})$ for the nitro group with S2p electron binding energies (E_b) for neutral *ortho* and charged *ortho*, *meta*, and *para* sulfur groups in substituted nitrobenzenes; ▲ *ortho*, △ *ortho* (charged), O *meta* (charged), ● *para* (charged).

the S2p electron binding energy for the sulfur substituents, excluding all substituents for which there were indications of a deviating reduction mechanism. The *para* substituted compounds give a good linear correlation. The *meta* substituted compounds do not fit this correlation but seem to give another correlation with a much smaller slope.

Since the σ_p^- constants apply, the reduction mechanism is susceptible to the $-M$ effect from sulfur substituents with strongly electro-negative oxygen directly attached to the sulfur (groups with $S=O$ bonds), and there is a significant difference between the half-wave potentials for this type of *meta* and *para* substituents. On the other hand in electron spectroscopy it was found that to a great extent the $-M$ effect is only relayed by the sulfur atoms in such groups.[2b] Hence a $-M$ conjugation has only a negligible effect, and the *para* and *meta* groups have very similar binding energies. Therefore the mechanistic difference between the reduction of the *para* and *meta* compounds comes to light here in view of the fact that two different correlations are obtained for the *para* and *meta* substituents. It can thus be concluded that the binding energies of sulfur in the sulfur groups mainly reflect their inductive substituent effect.

In Fig. 2 the data for compounds with charged substituents and the *ortho* substituents have been plotted together with the regression lines for the *para* compounds. The charged substituents clearly deviate, and the previously observed repulsion effect of the charge on the anions causing their reduction potentials to become more negative than normal comes clearly to light. One observes, however, that at pH 5, where the sulfinate substituted compound is probably reduced at the positive side of the electro-capillary zero, the points for this substituent are situated nearer to the regression line. The *ortho* compounds show a poor correlation. Since binding energies are generally not sensitive to steric effects, this may be an indication that steric *ortho* effects are operative in the polarographic reduction.

The polarographic half-wave potentials reflect the ease of uptake of the second electron in the reduction of the nitro group, and is a function of the rate constant for the heterogeneous electrode process.[1] The correlation of half-wave potentials with electron binding energy thus constitutes the first example of a correlation between core electron binding energies and reactivity data.

Polarographic reduction mechanism of nitrobenzenethiols. The correlation of the thiols is particularly interesting. At pH 7.2 and 9.3 one would expect them to be reduced as anions. However, their half-wave potentials are shifted too much in a positive direction to be consistent with the binding energies of the thiolates, whereas the binding energies of the thiols fit the correlations very well. If the correlation with binding energies has any relevance, which we think it has, this is an indication that the thiol substituted compounds are not reduced as anions. The results obtained in the previous polarographic investigation [2a] would be in accordance with a reduction of the nitro group under the influence of a mercury compound formed by a currentless fission of the disulfide which is generated by anodic or spontaneous oxidation of the thiols.

The binding energies have previously been shown to correlate very well with the charges on atoms in molecules, which are estimated as the sum of the partial ionic character of bonds as a function of the electronegativity

difference between the atoms forming each bond. Since the electronegativity of mercury is very similar to that of hydrogen, the binding energy of sulfur in the mercury compound would be very similar to that of the thiol. Hence the good correlation with the thiol binding energy at higher pH values can be well explained, if the reduction of the nitro group occurs at a less negative potential than the reduction of mercury compound.

Correlation of S2p binding enrgies with inductive substituent constants. The conclusion made above that the binding energies of sulfur reflect the inductive substituent effects of the sulfur groups is further substantiated by Fig. 3, in
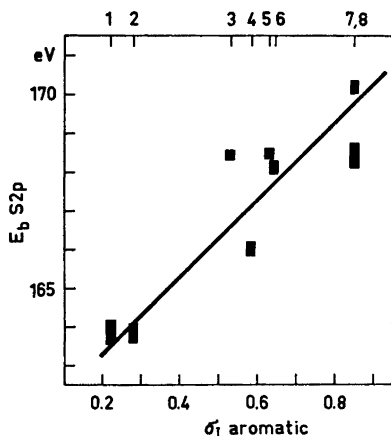

Fig. 3. Correlation of S2p electron binding energies (E_b) with aromatic inductive substituent constants (σ_I) for some sulfur groups in substituted nitrobenzenes (1 $-SCH_3$, 2 $-SH$, 3 $-SO_2NH_2$, 4 $-S(O)CH_3$, 5 $-SO_2OCH_3$, 6 $-SO_2CH_3$, 7 $-SO_2Cl$, 8 $-SO_2F$).
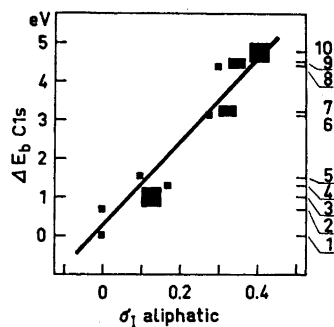
Fig. 4. Correlation of C1s electron binding energy shifts (ΔE_b) with aliphatic inductive substituent constants (σ_I) for the group R in RCH$_3$ (1 $-CH_3$, 2 $-CH_2NH_2$, 3 $-CH_2Br$, 4 $-CH_2Cl$, 5 $-CH_2OH$, 6 $-COCH_3$, 7 $-CHO$, 8 $-COOR$, 9 $-COOH$, 10 $-CCl_3$).

which the binding energies have been plotted against σ_I constants (σ_I: $-SH$ 0.28, $-SCH_3$ 0.22, $-S(O)CH_3$ 0.58, $-SO_2CH_3$ 0.64, $-SO_2NH_2$ 0.53, Ref. 3; $-SO_2OCH_3$ 0.63, $-SO_2Cl$ 0.86, $-SO_2F$ 0.86, Ref. 4). A good linear correlation is obtained. This fact together with the fact that separate lines are obtained for the *para* and *meta* substituents in the correlation of half-wave potentials with binding energies implies that the $-M$ effect observed in the polarographic reduction of the nitro group is some simple function of the inductive effect of the $-M$ substituent.

It would be highly desirable to investigate the general validity of these conclusions by including some reaction series with a greater number of substituents and also with other elements. In Fig. 4 the C1s electron binding energy shifts of carbon in groups bound to $-CH_3$ from Ref. 5 (groups Nos. 3 and 7 from Ref. 11), have similarly been plotted against aliphatic σ_I constants. (σ_I: $-CH_3$ 0, $-CH_2NH_2$ 0, $-CH_2OH$ 0.10, $-CH_2Cl$ 0.17, $-COCH_3$ 0.28, $-COOR$

0.30, Ref. 4; $-CH_2Br$ 0.12, $-CHO$ 0.31, $-COOH$ 0.34, $-CCl_3$ 0.40, Ref. 3.)
A similar correlation as that in Fig. 3 is obtained. This constitutes further
support for the conclusion that the binding energies reflect the inductive
substituent effects.

IR SPECTROSCOPY

Correlation with σ constants. As already mentioned, IR frequencies some-
time correlate with Hammett substituent constants, and there are examples
of well established cases in the literature (for references see Ref. 6). In the
case of substituted nitrobenzenes there are contradictory data in the literature.
Kross and Fassel found a good correlation of the asymmetric NO stretching
vibrations with Hammett σ constants for a number of *para* substituted nitro-
benzenes measured in bromoform solution.[7] Ghersetti found a good correla-
tion for some sulfur substituted nitrobenzenes with σ^+ constants in chloro-
form,[8] whereas Hamer *et al.* in a recent investigation on a large number of
meta and *para* substituted nitrobenzenes in KBr pellets found a poor correla-
tion with σ constants.[9]

In the present investigation the series of Kross and Fassel was extended
by measuring the NO stretching vibrations for a series of *meta* substituted

Table 2. NO stretching vibrations in substituted nitrobenzenes, measured in 1 % bromo-
form solution.

Substituent	σ (Ref. 4)	ν_{NO_2} asym.	ν_{NO_2} sym.	Ref.
None	0	1521	1344	
p-N(CH₃)₂	−0.83	1486, 1519	1319	
m-NH₂	−0.16	1524	1348	
p-NH₂	−0.66	1507	1336	7
p-OCH₃	−0.27	1514	1340	7
m-OH	0.12	1526	1347	
p-OH	−0.37	1513	1342	
p-CH₃	−0.17	1517	1347	7
m-Cl	0.37	~1521, ~1533	1346	
p-Cl	0.23	1526	1348	7
m-Br	0.39	1529	1345	
p-Br	0.23	1527	1352	7
p-I	0.18	1526	1349	7
m-COOH	0.37	1533	1346	
p-COOH	0.45	1537	1350	7
p-COOCH₃	0.45	1530	1352	7
m-CHO	0.35	1535	1348	
p-CHO	0.22	1533	1348	7
m-CN	0.56	1536	1349	
p-CN	0.66	1528	1342	7
m-NO₂	0.71	1537	1343	
p-NO₂	0.78	1553	1343, 1362	7
p-CH₂Cl	0.18	1527	1351	7
p-CH₂CN	0.01	1523	1350	7
p-C₆H₅	−0.01	1518	1348	7
p-N=NC₆H₅	0.64	1530	1349	7

Table 3. S2*p* electron binding (E_b) and NO stretching vibrations in sulfur substituted nitrobenzenes, measured in 1 % bromoform solution.

No.	Substituent	E_b eV	σ (Ref. 4)	ν_{NO_2} asym.	ν_{NO_2} sym.
1	o-SH	164.1		1513	1336
2	p-SH	163.7	0.15	1512	1337
3	o-SCH$_3$	163.9		1521, 1529	1337
4	m-SCH$_3$	164.0	0.15	1525	1344
5	p-SCH$_3$	163.7	0.00	1507	1333
6	o-SC$_6$H$_4$CH$_3$	164.0		1508	1337
7	p-SC$_6$H$_4$CH$_3$	163.6		1508	1334
8	o-SC$_6$H$_4$NO$_2$	164.2		1514, 1528	1335
9	p-SC$_6$H$_4$NO$_2$	163.7		1519	1340
10	o-SSC$_6$H$_4$NO$_2$	164.1		1511	1336
11	m-SSC$_6$H$_4$NO$_2$	163.8		1524	1344
12	p-SSC$_6$H$_4$NO$_2$	163.7		1518	1339
13	p-SSO$_2$C$_6$H$_4$NO$_2$	164.0		1531	1343
14	o-SNH$_2$	164.3		1508	1337
15	o-SCl	164.1		1498, 1512	1328
16	o-SOCH$_3$	165.2		1505	1337
17	o-S(O)CH$_3$	166.0		1525	1342
18	m-S(O)CH$_3$	166.0	0.52	1534	1348
19	p-S(O)CH$_3$	165.9	0.49	1525	1342
20	o-S(O)C$_6$H$_4$NO$_2$	166.2		1532	1343
21	p-S(O)C$_6$H$_4$NO$_2$	166.1		1525	1342
22	o-SO$_2$CH$_3$	168.1		1542	1324
23	m-SO$_2$CH$_3$	168.0	0.60	1533	1346
24	p-SO$_2$CH$_3$	168.2	0.72	1533	1314, 1328, 1347
25	o-SO$_2$C$_6$H$_5$	—		1545	1328
26	p-SO$_2$C$_6$H$_5$	167.8	0.71 [3]	1530	1348
27	p-SO$_2$C$_6$H$_4$NO$_2$	167.9		1534	—
28	p-SO$_2$SC$_6$H$_4$NO$_2$	168.2		1531	1343
29	m-SO$_2$NH$_2$	168.4	0.46	~1533	~1350
30	o-SO$_2$Cl	168.7		1547	1359
31	m-SO$_2$Cl	168.2		1537	1348
32	p-SO$_2$Cl	168.5		1536	1347
33	p-SO$_2$F	170.2		1536	1320
34	o-SOO$^\ominus$	166.0		1522	1346
35	m-SOO$^\ominus$	165.9	−0.02	1524	1347
36	p-SOO$^\ominus$	166.0		1518	1340
37	o-SOOCH$_3$	167.4		1530	1343
38	m-SOOCH$_3$	167.2	0.66 [1]	1529	1346
39	p-SOOCH$_3$	167.5		1526	1341
40	o-SO$_3^\ominus$	168.3		1538	—
41	m-SO$_3^\ominus$	168.3	0.38 [10]	1538	1348
42	p-SO$_3^\ominus$	168.2	0.15 [10]	1523	1346
43	o-SO$_2$OCH$_3$	168.5		1545	~1364
44	m-SO$_2$OCH$_3$	168.4	0.71 [1]	1533	1347
45	p-SO$_2$OCH$_3$	168.4		1531	1346

compounds in bromoform. The results are given in Table 2, which shows the data for the common substituents. The series of sulfur compounds was also measured, and Table 3 shows the data together with the S2*p* binding energies for these substituents.
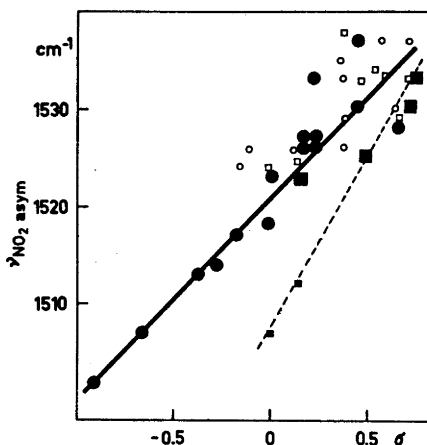
Fig. 5. Correlation of asymmetric NO stretching vibrations with σ constants for substituted nitrobenzenes. ■ para (sulfur groups), □ meta (sulfur groups), ● para, ○ meta.

In Fig. 5 the asymmetric NO stretching vibration has been plotted against the σ constants for all meta and para groups for which these constants were available. Only a rough correlation is obtained, and some sulfur substituents cause large deviations. It is not improved by employing the σ^- or σ^+ constants, but is better than the correlation of Hamer et al. The elimination of the solid state effects by measuring in solution thus improves the result. The correlation is, however, too poor to be used for the estimation of σ constants for sulfur groups as originally intended.

In a previous investigation the correlations of the asymmetric stretching vibrations of CO in the isoelectronic carboxyl group [12] and of SO in the "iso-valent" sulfinate group [13] with σ constants have been studied and compared. The sulfinate group as well as the sulfonate group gave better correlations than the carboxylate group, the correlation of which is as poor as the present one. However, if the asymmetric NO vibrations are plotted against the asymmetric CO vibrations from Ref. 12, a good linear correlation is obtained, indicating that the vibrational behaviour of these groups are very similar. Recently a more detailed study of carboxylate vibrations has appeared,[14] which arrives at a similar result, and shows a $\nu_{CO} - \nu_{NO}$ plot including more substituents. From these investigations it appears that the condition for correlations of vibrations with σ constants in substituted aromatic compounds is that they are insulated from the aromatic ring by mass, bond strength, or symmetry.

In the present correlation, the p-SH and p-SCH$_3$ substituents show large deviations, and the deviation of p-SCH$_3$ is not eliminated by using the σ^+ constants. In the light of the mentioned conditions, this fact can be understood, if one assumes that the known $+M$ effect of bivalent sulfur substituents [15] is of a greater strength than that of substituents with first row elements. This will cause differences in the bond order and bond strength between the nitro group and the aromatic ring, invalidating the requirements for good correlations. If the para sulfur groups are singled out and correlated separately (dotted line in Fig. 5) there is some indication of a better correlation, although the number of substituents is scanty.
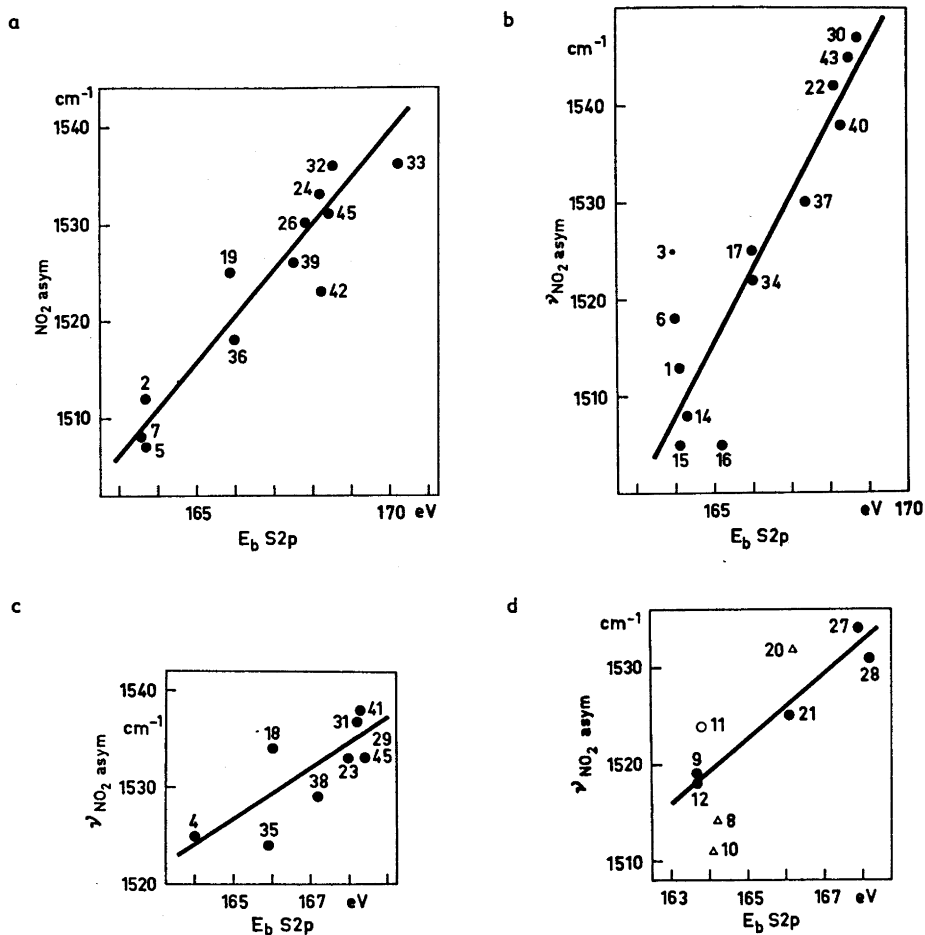
Fig. 6. Correlation of asymmetric NO stretching vibrations with S2*p* electron binding energies (E_b) of sulfur groups for nitrobenzenes substituted with a) simple *para* sulfur groups; b) simple *ortho* sulfur groups; c) simple *meta* sulfur groups; d) nitrophenyl sulfur groups (bis-nitrophenyl compounds); △ *ortho*, ○ *meta*, ● *para*.

*Correlation with S2*p* binding energies.* In Fig. 6 a—d, the asymmetric NO stretching vibration has been correlated with the S2*p* electron binding energies of the sulfur substituents. The *ortho*, *meta*, and *para* compounds were treated separately. Most of the mono nitro substituted *para* compounds give a fairly good correlation (Fig. 6a). The corresponding *ortho* compounds also give a fairly good correlation with a greater slope, except for those in which sulfur carries a lone *p*-electron pair (Fig. 6b). For such groups there has been some indication of a neighbouring group effect between the oxygen in the nitro group and sulfur,[2b] and it seems probable that the irregularities in Fig. 6b

could be partly due to such an effect. The *meta* compounds give a smaller slope than the *para* compounds (Fig. 6c), which parallels the behaviour of the half-wave potentials. The bis-nitrophenyl substituted compounds have been treated separately in Fig. 6d. They give a smaller slope than the *mono* nitrophenyl substituted compounds, but the number of compounds is too small to allow any significant conclusion.

The binding energies cover a comparatively large range of shifts ($\sim$7.5 eV), and the correlations are similar to the one in Fig. 5. This fact seems to imply that the S$2p$ binding energies of the sulfur groups at least qualitatively can serve as a description of their substituent effects on the asymmetric $\stackrel{\dots}{N}O$ stretching vibrations. Particularly the correlation with the mono nitro substituted *para* groups in Fig. 6a is consistent with this idea. Together with the indication in the preceding paragraph of a better correlation with σ constants, if the sulfur substituents are singled out and correlated separately, this leads to the suggestion that correlations of vibration data with substituent parameters will probably be more useful, if only substituents are used, in which the same element links it to the aromatic ring. Because of the chemical versatility and polyvalency of sulfur, this element is very useful for such series of "homo-elemental" substituents, and it seems urgent that substituent constants should be determined for as many sulfur groups as possible.

CONCLUSION

It is obvious that a correlation exists between the S$2p$ electron binding energies and certain physico-chemical parameters of the nitro group in sulfur substituted nitrobenzenes. There is also evidence that the S$2p$ electron binding energies of sulfur groups as well as C$1s$ electron binding energies in carbon groups parallel the inductive substituent constants of these groups fairly well. These results give the impression that the ESCA shifts of the linking atom in substituent groups (ESCA group shifts) could be of value as a new approach to the study of substituent effects in organic chemistry, which may be well worth future investigation.

EXPERIMENTAL

Polarography. The experimental details are described in Ref. 1. The bis-nitrophenyl substituted compounds have such a low solubility in the media used in Ref. 1 that they could not be measured satisfactorily.

ESCA spectra. The experimental details are given in Ref. 2a.

IR spectra. The IR spectra were recorded with a Unicam SP 200 spectrophotometer in 1 % bromoform solution using a 0.212 mm sodium chloride cell. The calibration was made against polystyrene.

Chemicals. The nitrobenzenes substituted with common substituents were commercial reagents of the best quality available. When not *p.a.* quality they were recrystallized or redistilled until they showed satisfactory data. Compounds Nos. 29, 30, and 32 were recrystallized commercial reagents. The preparation of compounds Nos. 31, 34—36 is described in Ref. 16, and that of Nos. 37—45 in Ref. 1. (The numbering is made according to Table 3.) Most of the compounds described in the following were checked by elemental analysis.

o- and p-*Nitrobenzenethiols* were prepared according to Bennett and Berry [17] by treating the chloronitrobenzenes with sodium sulfide in aqueous ethanol. M.p. *ortho* 58—59° (lit. 56, 58, 61° [18a]), *para* 76—77° (lit. 77° [18a]).

m-*Nitrobenzenethiol* was prepared according to Bennett and Berry [17] by treating diazotized *m*-nitroaniline with potassium xanthate. It was isolated as the potassium salt.

Methyl o-, m-, and p-nitrophenyl sulfides were prepared by treating the nitrobenzenethiols with methyl iodide in aqueous alkali.[19] M.p. *ortho* 62.5—63.5° (lit. 64, 65° [18b]), *para* 70.5—71.5° (lit. 72° [18b]). Found for *meta*: C 49.7; H 4.3; N 8.2; S 18.8. Calc. for $C_7H_7NO_2S$: C 49.7; H 4.1; N 8.2; S 18.8.

Methyl o-, m-, and p-nitrophenyl sulfoxides were prepared by oxidation of the sulfides with 10 % peracetic acid in acetone with cooling.[20] The products were recrystallized from ethanol. M.p. *ortho* 100—101° (lit. 101—102° [21]), *meta* 119—120° (lit. 117—118° [22]), *para* 147—148° (lit. 148—149° [22]).

Methyl o-, m-, and p-nitrophenyl sulfones were prepared by oxidation of the sulfides with hydrogen peroxide in boiling glacial acetic acid according to Claasz.[23] M.p. *ortho* 104—105° (lit. 104—105°,[19] 106° [23]), *meta* 145—146° (lit. 146° [24]), *para* 139—141° (lit. 142—145° [25]).

o-*Nitrophenyl phenyl sulfides* were prepared by treating the chloronitrobenzenes with thiophenol in alkaline aqueous ethanol.[26a] M.p. *ortho* 79.5—81.5° (lit. 77, 80.5° [18b]), *para* 54—55° (lit. 55, 57° [18b]).

o-*Nitrophenyl phenyl sulfone* was prepared by oxidation of the sulfide with chromic acid in acetic acid.[25] M.p. 146.5—147° (lit. 147.5° [27]).

p-*Nitrophenyl phenyl sulfone* was prepared by oxidation with potassium permanganate in acetone-acetic acid at room temperature.[26b] The pH was kept at 7 by addition of 5 N sulfuric acid with a pH-stat. M.p.: 141—143° (lit. 142°[25], 143° [27]).

o- and p-*Nitrophenyl p-tolyl sulfides* were prepared by treating the chloronitrobenzenes with *p*-toluenethiol in alkaline aqueous ethanol.[26a] M.p.: *ortho* 87—89° (lit. 87.5, 90° [18b]), *para* 81—82° (lit. 81, 82° [18b]).

Bis(o-nitrophenyl) sulfide was prepared by treating *o*-dinitrobenzene with sodium sulfide in aqueous ethanol.[28] M.p. 122—122.5° (lit. 122, 123° [18c]).

Bis(p-nitrophenyl) sulfide was prepared according to Price and Stacey [29] by treating *p*-chloronitrobenzene with potassium xanthate. M.p.: 159—161° (lit. 158—160°).

Bis(o- and p-nitrophenyl) sulfoxides were prepared according to Lobry de Bruyn and Blanksma.[30] M.p.: *ortho* 183.5—184° (lit. 184°), *para* 179—180° (lit. 178, 187° [31]).

Bis(p-nitrophenyl) sulfone was prepared by oxidation of the sulfide with chromic acid in acetic acid.[25] M.p. 280—282° (lit. m.p. varies in the range 260—290° [31]). (Found: S 10.5. Calc. for $C_{12}H_8N_2O_6S$: S 10.4.)

Bis(o-nitrophenyl) disulfide was prepared according to Bogert and Stull [32] by treating the *o*-chloronitrobenzene with sodium sulfide in ethanol. M.p. 193—196° (lit. 192—195°).

Bis(p-nitrophenyl) disulfide was isolated either from a commercial reagent or from a product prepared as the *ortho* disulfide, which both were impure mixtures of disulfide and monosulfide.[33,34] The disulfide was separated from the monosulfide by extracting the mixture with hot benzene and recrystallizing the residue twice from xylene and washing with ethanol. M.p. 181—183° (lit. 180, 181, 182, 184° [18b]). (Found: S 20.7. Calc. for $C_{12}H_8N_2O_4S$: S 20.8.)

Bis(m-nitrophenyl) disulfide was prepared according to Sheppard [35] by reduction of *m*-nitrobenzenesulfonyl chloride with hydroiodic acid. M.p. 81.5—83° (lit. 82—83°).

p-*Nitrophenyl p-nitrobenzenethiolsulfonate* was prepared according to Vinkler and Klivényi [36] by oxidation of bis (*p*-nitrophenyl) disulfide with perbenzoic acid in chloroform. M.p. 181—183° (lit. 180°).

o-*Nitrobenzenesulfenyl chloride* was prepared according to Hubacher [37] by chlorinolysis of bis (*o*-nitrophenyl) disulfide in carbon tetrachloride. M.p. 74—75° (lit. 73—74.5°).

o-*Nitrobenzenesulfenyl amide* was prepared according to Zincke and Farr [31] by ammonolysis of *o*-nitrobenzenesulfenyl chloride in chloroform. M.p. 123.5—125° (lit. 124—125°).

Methyl o-nitrobenzenesulfenate was prepared according to Zincke and Farr [31] by treating *o*-nitrobenzenesulfenyl chloride with sodium methylate in methanol. M.p. 52—53.5° (lit. 54°).

p-*Nitrobenzenesulfonyl fluoride* was prepared by treating *p*-nitrobenzenesulfonyl chloride with excess potassium fluoride [36] in dilute aqueous ethanol. M.p. 76—77° (lit. 77.5—78.5°).

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