40. *The Mesomeric Effect of the Sulphoxide Group.*

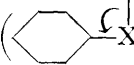By D. Ll. Hammick and R. B. Williams.

The electric dipole moment of di*iso*butyl sulphoxide has been determined in benzene solution. Its value, 3·90 D., is less than that of diphenyl sulphoxide, 4·08 D., and hence the mesomeric effect of the sulphoxide group is negative. This should lead, on the electronic theory of benzenoid reactivity, to the expectation of attack by kationoid reagents in the *o*, *p*-positions in the benzene nucleus and by anionoid reagents in the *o*, *m*-positions. Owing to the fragility of the sulphoxide group, the first expectation could not be tested; the fact, however, that *p*-iododiphenyl sulphoxide is hydrolysed by alkali under conditions where the m-*iodo*-derivative is unaffected fulfils the second prediction.

It is shown that the charges on the sulphur, nitrogen, and iodine atoms in the sulphoxide, nitroso- and iodoxy-groups are positive; these groups are alike in respect to their inductive and mesomeric affects, which are negative and positive respectively.

THE introduction of an atom or group X into the benzene molecule in place of a hydrogen atom produces a mesomeric effect M (Robinson, *J. Soc. Dyers Col.*, 1934, 65; Ingold,

Chem. Reviews, 1934, **15**, No. 2). The sign of M can be found from a comparison of the electric dipole moments of the corresponding alkyl and aromatic compounds with the substituent X (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668). Where data are not available for making this comparison, the sign of the mesomeric effect can be inferred from the orienting effect of X on further substitution in the benzene nucleus, because the Robinson theory of the orienting process requires o, p-reactivity towards kationoid reagents for a $+ M$ effect and o, m-reactivity for a $- M$ effect.

Those atoms and groups which produce a $+ M$ effect fall into two classes. In the first, comparatively small, category, we find the alkyl groups and certain anionic centres such as $-\bar{O}$ (phenoxide ion), where the inductive and the mesomeric effect are both positive. In the second, we have atoms and groups in which, although the inductive effect is negative, the mesomeric effect is positive and dependent on covalency increase on the atom attached to the nucleus $\left(\bigotimes\!\!-\!\!X, \text{where } X = -NR_2, -OR, \text{halogens, etc.}\right)$. This tendency for covalency increase to occur, with accession of electrons into the nucleus in spite of an opposing inductive effect, is so prevalent that special interest attaches to the few cases where the general rule is not obeyed. The first exceptional case was established for the nitroso-group, the electric dipole moment of nitrosobenzene being found to be greater than that of nitrosodimethylhexane by 0·63 D. (Hammick, New, and Sutton, J., 1932, 742). The existence of the $-M$ effect, due presumably to a tendency to covalency decrease $-N\!\!=\!\!O$, was confirmed by the fact that o- and p-bromonitrosobenzenes are readily hydrolysed by aqueous silver nitrate (Hammick and Illingworth, J., 1930, 2358). According to the Robinson theory of benzenoid reactivity, a $-M$ effect will facilitate attack by anionoid reagents (NO_3^-, OH^-) in the o- and p-positions.

The second exception is the iodoxy-group, $-IO_2$. Whatever the structure of this group may be, there must be at least two unshared electrons on the iodine atom. Nevertheless, nitration of iodoxybenzene (Masson, Race, and Pounder, J., 1935, 1669) occurs in the m-position and hence the mesomeric effect must be negative.

We have found in the sulphoxide group, $>S\!-\!O$, a third case of a substituent with unshared electrons on the atom next to a benzene nucleus exerting a negative mesomeric effect. We find that the dipole moment of diphenyl sulphoxide is greater than that of di*iso*butyl sulphoxide,* the negative sign of the mesomeric effect leading to the expectation of attack by kationoid reagents in the m,o-positions in the aromatic sulphoxide. It has not been possible to verify this prediction by direct experiment owing to the inability of the reactive sulphoxide group to withstand the drastic conditions necessary for m,o-substitution by kationoid reagents. We find, however, that p-iododiphenyl sulphoxide is hydrolysed by sodium hydroxide under conditions in which the m-*iodo*-derivative is unaffected.

<div align="center">EXPERIMENTAL.</div>

<div align="center">*The Electric Dipole Moment of Di*iso*butyl Sulphoxide.*</div>

The method and apparatus described by Sutton (*loc. cit.*) were used, benzene being the solvent.

Preparation of Materials.—Di*iso*butyl sulphoxide. This was prepared from di*iso*butyl sulphide, which was obtained from *iso*butyl alcohol by Beckmann's method (*J. pr. Chem.*, 1878, **17**, 445) with two modifications. First, a mixture of oleum and concentrated sulphuric acid was used instead of the latter alone for converting the *iso*butyl alcohol into the acid sulphate, for it was found that without the oleum much of the alcohol remained unchanged. Secondly, the crude di*iso*butyl sulphide was washed with concentrated potassium hydroxide solution in order to get rid of *iso*butyl mercaptan, formed as a by-product, and then with water, instead of only with water.

The sulphoxide was prepared from the sulphide by oxidation with nitric acid (Beckmann,

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* This was chosen as the aliphatic sulphoxide most suitable for dipole-moment measurements, because it has a higher m. p. (68°) than most aliphatic sulphoxides and hence is more easily purified. It is, moreover, not hygroscopic as are many aliphatic sulphoxides.

loc. cit.), the crude product being purified by extraction with ligroin (b. p. 40—60°); m. p. 68·0° (Beckmann, *loc. cit.*, gives 68·5°).

Benzene. A. R. Benzene, thiophen-free, was purified, dried, and distilled according to Hampson, Farmer, and Sutton (*Proc. Roy. Soc.*, 1933, A, 143, 147).

Results.—The results of the measurements, at 25° in benzene solution, are given in the table, where the symbols have their usual significance; the refractive indices relate to the mercury green line 5461. To minimise errors in the densities, the experimental values were plotted against f_2, the values used in the calculations and given in the table being obtained from the mean line.
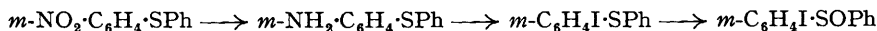
$f_2.$	$d.$	$\epsilon.$	$n^2.$	$P_2.$	$_EP_2.$
0·00427	0·87415	2·36323	2·25604	359·01	48·70
0·00288	0·87404	2·33378	2·25632	360·91	48·37
0·00196	0·87397	2·31427	2·25672	361·50	49·48
0·00149	0·87394	2·30416	2·25675	360·59	48·71
0·00000	0·87382	2·2727	2·25712	—	—

At $f_2 = 0$, $P_2 = 364·0$ c.c. and $_EP_2 = 48·8$ c.c., whence $P_2 - {}_EP_2 = 315·2$ c.c. and $\mu = 3·90.$*

The Action of Hydroxyl Ions on m- *and* p-*Iododiphenyl Sulphoxides.*

Preparation of Materials.—p-*Iododiphenyl sulphoxide.* The method of Willgerodt and Klinger (*J. pr. Chem.*, 1912, 85, 308) was employed.

m-*Iododiphenyl sulphoxide.* This substance, not hitherto described, was prepared from m-*nitrodiphenyl sulphide* according to the scheme :

$$m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SPh} \longrightarrow m\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SPh} \longrightarrow m\text{-C}_6\text{H}_4\text{I}\cdot\text{SPh} \longrightarrow m\text{-C}_6\text{H}_4\text{I}\cdot\text{SOPh}$$

Crude m-nitrodiphenyl sulphide, prepared from m-nitroaniline and sodium thiophenoxide according to the method described by Weedon and Doughty for o-methyldiphenyl sulphide (*Amer. Chem. J.*, 1905, 33, 386), was steam-distilled for 65 hours, the distillate extracted twice with ether, and the combined extracts dried over calcium chloride. The brown oil left after removal of the ether solidified on cooling in a freezing-mixture and scratching. It was purified by extracting it twice with ligroin (b. p. 40—60°) at room temperature, about 80—90% being dissolved altogether, and cooling the extracts in a freezing-mixture in the presence of a seeding crystal. Vigorous scratching caused the m-nitrodiphenyl sulphide to separate as a pale yellow solid, which was filtered off, washed with ligroin (b. p. 40—60°), which had previously been cooled in a freezing-mixture, and dried in the air on a porous plate. Concentration and cooling of the mother-liquors yielded a further quantity of substance. 50·9 G. of m-nitroaniline and 43·3 g. of thiophenol gave 17·9 g. of this product. A further two extractions with ligroin of a portion of this product afforded the pure substance as pale yellow crystals, m. p. 42·5° (Found : S, 13·83; N, 5·88. $C_{12}H_9O_2NS$ requires S, 13·85; N, 6·06%).

8 G. of this sulphide were converted by reduction with stannous chloride and hydrochloric acid (cf. Mauthner, *Ber.*, 1906, 39, 3593) into 5·7 g. (82% yield) of crude m-aminodiphenyl sulphide (an oil, solidifying in a freezing-mixture). This was converted by diazotisation and treatment with potassium iodide (cf. Willgerodt and Klinger, *loc. cit.*) into 3·7 g. of crude m-iododiphenyl sulphide (colourless oil). This was oxidised, with perhydrol in glacial acetic acid, to the sulphoxide (cf. Bergmann and Tschudnowsky, *Ber.*, 1932, 65, 457). The crude product (3·4 g.; 88% yield) was purified by extraction with boiling ligroin (b. p. 60—80°) until about 90% had been dissolved. The solid separating on cooling in a freezing-mixture was recrystallised from 50% alcohol with norit, and finally from ligroin (b. p. 60—80°); colourless needles (1·6 g.), m. p. 73·5° (Found : S, 9·79. $C_{12}H_9OIS$ requires S, 9·76%).

Hydrolysis of p- *and* m-*Iododiphenyl Sulphoxide.*—Solutions of each of the isomers in equal concentration (0·3 g. in 30 c.c. of N/5-aqueous alcoholic potash, containing 60% alcohol by volume) were refluxed for 1 hour on the water-bath. After this treatment, the solution of the p-isomer was found to contain iodine ions, which were absent from the other solution.

DISCUSSION OF RESULTS.

The value obtained for the electric dipole moment of di*iso*butyl sulphoxide, 3·90, is numerically less than the moment of diphenyl sulphoxide, for which the following values

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* All dipole moments in this paper are given in Debye units (e.s.u. $\times$ 10⁻¹⁸).

P

are available : 4·08 (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397), 4·17 (de Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888), 3·99 (Hampson, Farmer, and Sutton, *loc. cit.*). That the sense of the dipole of the diphenyl sulphoxide molecule is as shown, $(C_6H_5)_2\overset{+\longrightarrow}{SO}$, follows from the fact that its value, 4·08, the mean of the three values quoted above, is greater than that, 2·57, of pp'-dichlorodiphenyl sulphoxide (Hampson, Farmer, and Sutton, *loc. cit.*). Hence the algebraic difference between the dipoles of the aliphatic and the aromatic sulphoxides is — 0·18, and this is a measure of the mesomeric effect of the sulphoxide group. A negative (outward) mesomeric effect means that the electromeric changes that occur on suitable activation will render the aromatic nuclei susceptible to attack by kationoid reagents in the *o*- and *p*-positions and by anionoid reagents in the *o*- and *m*-positions. The removal of iodine as ions from *p*-iododiphenyl sulphoxide by the action of hydroxyl ions, the *m*-isomer being unaffected, confirms this prediction.

The rule given by Sidgwick ("The Co-valent Link in Chemistry," pp. 180—181) may be put in a slightly more general form by saying that, whenever the atom attached to the benzene nucleus has a residual positive charge, the atom (or group to which it belongs) is *m,o*-orienting towards kationoid reagents; and it has been pointed out (Masson, Race, and Pounder, *loc. cit.*) that the orientation rule due to Hammick and Illingworth (*loc. cit.*) " is valid as to directive effect of groups XY only so far as it may correctly imply which elements, X, in the Periodic Classification are positive to which elements Y." It is therefore to be expected that the atoms by which the iodoxy-, nitroso-, and sulphoxide groups are attached to benzene nuclei should be positive with respect to the nuclear carbon.

For the case of the nitroso-group an approximate numerical calculation of the charge on the nitrogen atom can be made. The dipole moment of nitrosobenzene is 3·14 (Hammick, New, and Sutton, *loc. cit.*); the angle between the C–N and the N=O link is, however, not known. Most probably it lies between 125·25°, the normal angle between a single and a double bond for a tetrahedral atom, and 150°. Again, although the dipole moment in the Ph–N link is known to be directed towards the nitrogen atom, its value is in doubt but probably lies between 0·4 and 1·4. Of these values, 0·2 is contributed by the H–C link para to the nitroso-group, so that the C–N link probably has a moment between 0·2 and 1·2. The N=O link moment, which is directed away from the nitrogen atom, and the value of the residual charge on the nitrogen atom, depend on the values taken for the angle between the C–N and N=O links and for the Ph–N moment. These data, in conjunction with the interatomic distances 1·48 and 1·21 A. for the C–N and the N=O link (these and other link lengths are computed from Sidgwick's values for atomic radii, *op. cit.*, p. 83) yield maximum and minimum values for the charge on the nitrogen atom of + 0·48e and + 0·15e.

In the case of the sulphoxide group a similar calculation yields a positive value for the charge on the sulphur atom; the dipole model is, however, too crude to be used with any confidence to make even approximate computations. We therefore make the reasonable inference that the separation of charge associated with the co-ordinate link will establish a positive charge on the sulphur atom due to the S→O link greater than any positive charge on the nuclear carbon atom that could result from separation of charge in the covalent C–S links.

Very similar considerations apply to the iodoxy-group. There can be little doubt but that the two iodine–oxygen links leave a positive charge on the iodine atom greater than the negative charge it receives as a result of its linkage to a carbon atom in the nucleus.

It thus appears that there are two classes of substituent which exert a negative (outward) inductive effect on a benzene nucleus. In the first class we have groups and atoms such as $-NH_2$, $-OR$, and the halogens, where the charge on the carbon atom in the nucleus is positive with respect to the atom next to it $(\underset{\delta+}{>}\overset{\delta-}{C}-\overset{\delta+}{N}H_2, \underset{\delta+}{>}\overset{\delta-}{C}-\overset{\delta+}{C}l, \underset{\delta+}{>}\overset{\delta-}{C}-\overset{\delta+}{O}-\overset{\delta-}{H})$. The second class contains the groups NO, IO_2, and SO, in which there is a positive charge on the nuclear carbon atom due to separation of charge in the links $\underset{\delta+}{>}\overset{\delta-}{C}-N, \underset{\delta+}{>}\overset{\delta-}{C}-I$ and

$\overset{\delta+}{>}\overset{\overset{\delta-}{\delta-}}{C}\overset{\delta+}{-S-}C<$ and $+$ charges also on the nitrogen, iodine, and sulphur atoms due to the polarisation of the links $\overset{\delta+}{N}\overset{\delta-}{=O}$, $\overset{\delta+}{I}\overset{\delta-}{=O_2}$ and $\overset{\delta+}{S}\overset{\delta-}{-O}$; thus $>\overset{\delta+}{C}\overset{\overset{\delta-}{\delta+}}{-N}\overset{\delta-}{=O}$, $>\overset{\delta+}{C}\overset{\overset{\delta-}{\delta+}}{-I}\overset{\delta-}{=O}$ and

$>\overset{\delta+}{C}\overset{\overset{\delta-}{\delta-}}{-S-}\overset{\delta+}{C}<$. But only the first group appears to be able to contribute electrons to

$\overset{}{\underset{O_{\delta-}}{\downarrow}}$

electromeric processes leading to *o, p*-activation towards kationoid reagents; the groups in the second class do not do this, and it appears reasonable to connect this fact with the presence of a net positive charge on the atom next to the nucleus.