[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY AND FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# The Electric Moments and Infrared Spectra of Some Derivatives of Phenyl Methyl Sulfone

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The electric moments of phenyl methyl sulfone, *m*-methylsulfonylbenzene and *m*- and *p*-methylsulfonyl substituted aniline, phenol, anisole and benzoic acid have been measured in solution at 25°. The group moment of the methylsulfonyl group, and the angle between it and the principal axis of the molecule, have been calculated from the moments of the *meta* derivatives. It is found that the observed electric moments of compounds in which the methylsulfonyl group is *para* to an amino, hydroxy or methoxy group are larger than calculated from group moments. These increments are interpreted as evidence for enhancement of resonance and support the conclusion, reached from other studies, that structures involving the use of five or six orbitals on the sulfur atom make an appreciable contribution to the ground state of the molecule. Similar, but slightly smaller, increments are observed for *p*-hydroxy and *p*-methoxyacetophenone. Increased intensities of infrared absorption were observed for *p*-methoxyphenyl methyl and vinyl methyl sulfones as compared to phenyl methyl, *m*-methoxyphenyl methyl and dibutyl sulfones. These results also support the view that the sulfone grouping can enter into resonance interactions with electron-donating groups in the ground state.

## Introduction

The ability of electron-donor groups, such as $H_2N$, HO and $CH_3O$ to exert conjugative effects with the methylsulfonyl group, $CH_3SO_2$, has been clearly demonstrated in the excited state by shifts in ultraviolet absorption spectra,[1] in ground states by acidity constant measurements,[2] and in transition states by reaction rate studies.[3] On the basis of the failure of the vibration frequency of the S–O bond to change when the methylsulfonyl group is conjugated with a phenyl group Barnard, Fabian and Koch[4] concluded that conjugation was not important in the ground level of sulfone molecules. Koch and Moffitt[5] reviewed the evidence concerning conjugation available at that time and showed that a molecular orbital calculation consistent with the view of negligible or weak conjugation of the methylsulfonyl group[5] could be made. Recently it has been shown[6] that changes in the intensity of infrared absorption can be successfully correlated with conjugative effects. Infrared intensity measurements and dipole moment measurements have now been applied to compounds of the type which revealed conjugative effects by acidity measurements[2] in order to gain further evidence on this question.

## Experimental

**Apparatus and Method for Dipole Moment Measurements.**—Electric moments were determined in benzene or dioxane solution at 25°. The apparatus used for measuring dielectric constants and densities has been described.[7] Measurements were made on a series of five or six solutions ranging from 0.0005 to 0.0020 in mole fraction solute. The molar polarizations $P_2$ of the solutes at infinite dilution were found by the method of Halverstadt and Kumler.[8] The constants $a$, $b$, $\epsilon_1$, $v_1$ and $P_2$ obtained for each compound are shown in Table I; the symbols have the same significance as those adopted previously.[7] The molar refractions calculated from empirical constants have been used for the distortion polarizations. The dipole moments calculated from these data are shown in Table I ($\mu$ obs.) along with the corresponding values calculated from the group moments and angles ($\mu$ calcd.). The probable error in the dipole moments is about $\pm 0.10$ *D*.

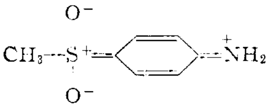
**Materials.**—The preparation of the solvents benzene and dioxane used in the dipole moment measurements has been described and their physical constants reported.[7] The sulfones were the samples used for the acidity constant measurements,[9] or were prepared by well-known methods.[9]

**Infrared Measurements.**—The integrated infrared absorption intensities for the symmetric SO stretching mode vibration at about 1150 cm.$^{-1}$ have been measured for the compounds listed in Table II. All measurements were made with carbon tetrachloride solutions in the concentration range 0.01 to 0.001 *M* with an absorption cell thickness of 1 mm. A Beckman Model 1R-2T instrument with rock salt optics and a slit width of 0.3 mm. was used. Some results were also checked on a Baird Associates instrument. For a set of curves representing three or four different concentrations of a given compound, a background trace of the pure solvent was superimposed and a point by point measurement of log $I_0/I$ was made at intervals of about 0.025 $\mu$. The results of the several concentrations were averaged, there being no noticeable failure of Beer's law, and these average absolute intensities are listed in Table II. In addition the extinction coefficient for the band maximum and the frequency of the band center are included.

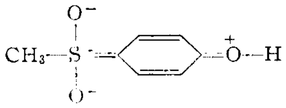
The absolute intensity results, in view of the deviations from the average value and the fit of the background solvent curve and variations in wing shapes, are considered to be relatively reliable to about 10%. While the extinction coefficients of the band maxima do not have any direct relation to the oscillating dipole, and therefore to the above argument, they are seen to parallel the integrated intensities.

## Discussion

**Dipole Moment Measurements.**—Appreciable contributions from structures such as I and II to the ground states of *p*-methylsulfonylaniline and *p*-methylsulfonylphenol, such as have been postulated,[2] should lead to an increased electric moment for the molecule above the value derived from group moments. We have, therefore, determined the electric moments of *m*- and *p*-methylsulfonyl sub-



I



II

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(1) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950); H. P. Koch, *J. Chem. Soc.*, 408 (1949).

(2) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952); F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 6019 (1953); H. J. Bacher and H. Kloosterziel, *Rec. trav. chim.*, **71**, 295 (1952).

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(4) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949).

(5) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

(6) G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

(7) M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

(8) I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

(9) We wish to thank P. J. Boutan for preparing some of these compounds.

TABLE I

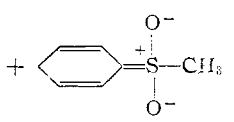
EMPIRICAL CONSTANTS,[a] MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS[b]

| Compound | $\epsilon_1$ | $a$ | $v_1$ | $b$ | $P_2$ | $MR_D$ | $\mu$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Obsd. | Calcd. |
| Phenyl methyl sulfone | 2.2730 | 31.37 | 1.14480 | −0.760 | 496.5 | 37.66 | 4.73 | 4.60 |
| Phenyl methyl sulfone (dioxane) | 2.2263 | 32.67 | 0.97212 | −0.383 | 504.2 | 37.66 | 4.77 | .. |
| *p*-Methylsulfonylaniline | 2.2725 | 52.30 | 1.14477 | −1.08 | 801.8 | 41.93 | 6.09 | 5.39 |
| *m*-Methylsulfonylaniline | 2.2734 | 36.80 | 1.14472 | −0.935 | 577.2 | 41.93 | 5.11 | 5.14 |
| *p*-Methylsulfonylphenol | 2.2715 | 39.73 | 1.14466 | − .953 | 620.6 | 40.05 | 5.32 | 4.91 |
| *m*-Methylsulfonylphenol | 2.2735 | 23.68 | 1.14478 | − .958 | 384.27 | 40.05 | 4.10 | 4.89 |
| *p*-Methylsulfonylbenzoic acid (dioxane) | 2.2215 | 35.00 | 0.97215 | − .620 | 545.2 | 43.81 | 4.95 | 4.75 |
| *m*-Methylsulfonylbenzoic acid (dioxane) | 2.2246 | 29.45 | 0.97210 | − .650 | 463.8 | 43.81 | 4.53 | 4.85 |
| *p*-Methylsulfonylanisole | 2.2725 | 38.75 | 1.14470 | − .905 | 611.8 | 43.92 | 5.27 | 4.87 |
| *m*-Methylsulfonylanisole | 2.2725 | 31.80 | 1.14474 | − .916 | 509.5 | 43.92 | 4.77 | 4.83 |
| *m*-Methylsulfonylchlorobenzene | 2.2725 | 26.60 | 1.14470 | −1.032 | 431.9 | 43.62 | 4.36 | 4.42 |
| *p*-Hydroxyacetophenone | 2.2725 | 18.80 | 1.14491 | −0.723 | 304.8 | 38.61 | 3.61 | 3.34 |
| *m*-Nitrophenol | 2.2728 | 21.60 | 1.14488 | − .800 | 346.2 | 35.27 | 3.90 | 4.33 |
| *p*-Methoxyacetophenone | 2.2728 | 17.32 | 1.14485 | − .490 | 294.3 | 42.57 | 3.51 | 3.27 |

[a] The observed dielectric constants $\epsilon_{12}$, and specific volumes $v_{12}$, of the solutions were plotted graphically against mole fraction solute. The points fall on straight lines of slope $a$ and $b$, with intercepts at zero mole fraction $\epsilon_1$ and $v_1$, respectively. The molar polarizations at infinite dilution $P_2$ and the dipole moments $\mu$, are calculated from these constants. All dipole moments are in Debye units. [b] In benzene solution unless dioxane is specified. [c] See text.

stituted aniline, phenol and benzoic acid. Since *p*-methoxyacetophenone and *p*-hydroxyacetophenone would be expected to show a similar effect their moments have been measured for comparative purposes. The electric moments of phenyl methyl sulfone and of the various *meta* substituted derivatives were studied for comparison with the results obtained to provide data for calculation of group moments as well as to compare with the *para* derivatives.

The electric moment of phenyl methyl sulfone is nearly the same in benzene (4.73) as in dioxane solution (4.77). It lies between the values observed for dimethyl sulfone[10] (4.49) and diphenyl sulfone[10] (5.05). Since the moments of dimethyl sulfide (1.40) and diphenyl sulfide (1.50) are nearly equal, the increase in moment as methyl groups are replaced by phenyl groups may be attributed to a contribution of structures such as III to the ground state of the molecule.



III

The interpretation of the results on the remaining compounds requires a knowledge of the group moments and the angles between these and the axes of free rotation of the groups. While the assumption of free rotation is probably not a good one in some cases, there is not enough information available at present to make a more detailed analysis. We have calculated[11] a set of moments and angles for the groups occurring in these compounds from molecules where group interaction through resonance should be small. Thus the methylsulfonyl group moment ($m$ = 4.42), and the angle between this and the axis of rotation of the group ($\psi$ = 63°), were found from the moments observed for phenyl methyl sulfone and the *m*-methylsulfonyl derivatives. The angle is somewhat larger than calculated from simple geometry (55°) using the bond angles reported for dimethyl sulfone.[12] Other bond moments $m$ and angles $\psi$ are: amino ($m$ = 1.85, $\psi$ = 143°40′); hydroxy ($m$ = 1.60, $\psi$ = 108°40′); carboxyl, dioxane solutions, ($m$ = 1.74, $\psi$ = 90°); methoxy ($m$ = 1.35, $\psi$ = 115°25′); acetyl ($m$ = 2.61, $\psi$ = 47°20′); nitro ($m$ = 3.60, $\psi$ = 0°); and hydrogen ($m$ = 0.4, $\psi$ = 180°).

The electric moments computed from these group moments are shown in Table I ($\mu$ calcd.) for comparison with the measured moments ($\mu$ obsd.); as a result of the method used to derive the bond moments and angles, these calculated moments include the normal conjugation of each separate group with the benzene ring (structures of type III for the methylsulfonyl group). When the observed values are larger than the calculated ones by more than the experimental error (about 0.1 $D$) enhancement of resonance is indicated; the magnitude of the increment is taken as a measure of the importance of the contribution of structures such as I and II in which there is group interaction through resonance.

The increment (0.70) of the observed over the calculated electric moment of *p*-methylsulfonylaniline indicates a considerable contribution from structures such as I. The increment is larger than observed for *p*-aminoacetophenone (0.53), about the same as for *p*-aminobenzonitrile[13] (0.75), but smaller than in *p*-nitroaniline[10] (1.10). Similarly the increment for *p*-methylsulfonylphenol (0.41) is larger than that for *p*-hydroxyacetophenone (0.27) but smaller than for *p*-nitrophenol[10] (0.68); however, the increment calculated for *p*-methylsulfonylanisole (0.40) is about the same as those for *p*-nitroanisole[10] (0.40) and *p*-cyanoanisole[13] (0.47) and is only slightly larger than that for *p*-hydroxyacetophenone (0.24). It appears from these results that the *p*-methylsulfonyl group has a power of conjugation (represented by structures of type I or II) about equal to the cyano group, less than the

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(10) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948.

(11) For a typical calculation, see O. Fuchs, *Z. physik. Chem.*, **B14**, 335 (1931).

(12) M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

(13) B. C. Curran, THIS JOURNAL, **72**, 4575 (1950).

nitro group, but somewhat greater than the acetyl group. A small increment, scarcely larger than experimental error, is also observed for *p*-methylsulfonylbenzoic acid; this indicates that group interaction is not particularly important in this substance. The results support the conclusion reached by Bordwell and Cooper[2] from a study of acidity constants, but electric moment data indicate that conjugation is less important in *p*-acetyl- than in *p*-methylsulfonylaniline, phenol and anisole.

Electric moments calculated for *meta* derivatives using the above group moments and angles agree well with the observed values, in general. Where there is a discrepancy, the observed value is lower, hence adjustments of group moments to improve the agreement with the *meta* derivatives will increase the increments noted for the *para* derivatives. For this reason it is believed that the increments discussed above are significant despite the approximations involved in the calculations.

Rather large differences between the observed and calculated moments of *m*-methylsulfonylphenol, *m*-methylsulfonylbenzoic acid and *m*-nitrophenol may be a consequence of some restriction of group rotation in these molecules. Good internal hydrogen bonds are not possible from the geometry, but a direct field effect might tend to favor configurations in which the hydrogen of the hydroxyl group was nearest the nitro or methylsulfonyl group; such an effect would tend to lower the observed moment of each of the above compounds.

The electric moment of *m*-nitrophenol reported here is identical with that of Williams and Fogelberg[14] and our value for *p*-methoxyacetophenone (3.51) is in excellent agreement with that of Lutskii[15]; however, the moment of *p*-hydroxyacetophenone reported here is lower than that previously reported.[15]

**Infrared Measurements.**—The intensity of the symmetric stretching mode of the $SO_2$ group is proportional to the square of the oscillating dipole moment of the molecule for this vibration. It appears likely, from the electronic description of the group and by comparison with the carbonyl group, that symmetrically stretching the two S–O bonds will result in a more negative charge on the oxygen atoms while a symmetric compression of the bonds will produce the opposite effect. It then follows that the oscillating dipole associated with this vibration of the sulfone group can be enhanced by providing an alternate electronic structure which will be favored by stretching of the S–O bonds and which will provide an additional dipole moment increment in the direction $\overrightarrow{SO_2}$. Attachment of a conjugating group provides just such an effect.

The results summarized in Table II show that in the presence of a group capable of conjugation an enhancement of the intensity does occur. The effect is parallel to that found for a conjugated carbonyl group.[6] It follows, therefore, that the sulfone group does interact with a conjugating group and that the interaction can be here interpreted as an ordinary resonance effect.

The frequency shift of the absorption maximum which shows up for a similar set of carbonyl compounds does not occur with these sulfones as has been pointed out by Bernard, Fabian and Koch.[4] In view of the present evidence it seems necessary to assume that the expected resonance shift is being balanced by some other effect, such as an inductive one, or that the resonance between the sulfone and the adjacent group is different than in the carbonyl case. That an inductive effect may play a role in the position of the absorption band is shown by a table of carbonyl frequencies[6] where, when the atom adjacent to the carbonyl group is altered, the position of the carbonyl band has no relation to the carbonyl absorption intensity or the resonance energy of the molecule.

From the above data it is apparent that dipole moment and infrared intensity measurements both support the conclusion from acidity constant measurements[2] that the sulfone group is capable of entering into a conjugative interaction with electron-donating groups in the ground state.

TABLE II

THE FREQUENCIES AND EXTINCTION COEFFICIENTS AT BAND MAXIMA AND THE INTEGRATED ABSORPTION INTENSITY OF SOME SULFONES

| Sulfone | $\nu$ (cm.$^{-1}$) | $\frac{1}{C1}\ln\left(\frac{I_0}{I}\right)_{\max}$ (mole$^{-1}$ l. cm.$^{-1}$) | $\frac{1}{C1}\int\ln\frac{I_0}{I}\,d$ (mole$^{-1}$ l. cm.$^{-2}$) |
|---|---|---|---|
| Butyl | 1141 | $8.3 \times 10^2$ | $1.38 \times 10^4$ |
| Methyl vinyl | 1150 | 11.3 | 1.57 |
| Phenyl methyl | 1161 | 17.5 | 2.1 |
| *m*-Methoxyphenyl methyl | 1155 | 15.9 | 2.1 |
| *p*-Methoxyphenyl methyl | 1154 | 27.7 | 3.1 |

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[14] J. W. Williams and J. M. Fogelberg, THIS JOURNAL, **52**, 1356 (1930).

[15] A. E. Lutskii, *Zhur. Fiz. Khim.*, **23**, 361 (1949).