[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA AND THE DEPARTMENT OF CHEMISTRY OF SWARTHMORE COLLEGE]

The Ultraviolet Absorption Spectra of Organic Sulfur Compounds. IV. Substituted Phenyl Sulfones[1]

BY EDWARD A. FEHNEL[2] AND MARVIN CARMACK

The bathochromic displacement of the benzenoid absorption which is observed when a sulfonyl group is attached to the benzene ring has been attributed to resonance interactions between the sulfone function and the aromatic nucleus.[3,4,5] In order to extend our knowledge of the behavior of the sulfone function in this type of system, we have determined the ultraviolet absorption spectra of a number of *o*- and *p*-substituted phenyl sulfones, including methyl, hydroxyl, amino and nitro derivatives. The results not only appear to confirm the resonance interpretation of the phenyl–sulfone function interaction, but also lead to some interesting implications with regard to the stereochemical configuration of the sulfone group.

Discussion of Results

It is generally agreed that resonance interactions rather than simple inductive effects are responsible for the observed displacements of near-ultraviolet absorption maxima among substituted aromatic compounds.[6] As a result of a systematic study of the ultraviolet absorption spectra of numerous benzene derivatives, Doub and Vandenbelt[7] have recently established this concept on a semi-quantitative basis and have correlated the primary band[8] displacement with the direction and extent of resonance interaction between the substituent groups of *p*-disubstituted benzene derivatives. Thus it is observed that where two substituents of the same electrical character (*i. e.*, electron-withdrawing, $-M$, or electron-releasing, $+M$) are opposed, the primary band is displaced only slightly compared to that of the most displaced monosubstituted parent compound, while interaction between two substituents of different types gives rise to a marked bathochromic displacement relative to the most displaced monosubstituted parent compound. As a corollary to this phenomenon, a general rule has been proposed to describe the behavior of benzene derivatives having ionizable substituents: "Where ionization of a group attached to a benzene ring enhances the already existing tendency for electron transfer to or from the ring, the maximum of the primary band is shifted to longer wave length; where ionization diminishes this tendency, a shift to shorter wave length results."[7]

It is interesting to consider the absorption characteristics of the *p*-substituted phenyl sulfones in the light of these results. Extensive interaction between the substituent groups is apparent in the spectra of *p*-hydroxyphenyl methyl sulfone (Fig. 1) and *p*-aminophenyl methyl sulfone (Fig. 2), in which the first primary absorption bands occur at considerably longer wave lengths ($\lambda_{\max.}$ 239, 269 mμ, respectively) than in the parent monosubstituted compounds (phenyl methyl sulfone, $\lambda_{\max.}$ 217 mμ[3]; phenol, $\lambda_{\max.}$ 211 mμ[7]; aniline, $\lambda_{\max.}$ 230 mμ[7]). These displacements are of the same magnitude as those observed by Doub and Vandenbelt[7] for the corresponding substituted benzoate anions (*p*-hydroxybenzoate anion, $\lambda_{\max.}$ 245 mμ; *p*-aminobenzoate anion, $\lambda_{\max.}$ 265 mμ), which would seem to bear out the previously proposed[3] analogy between the sulfonyl and carboxylate functions.

On formation of the phenolate anion by solution of *p*-hydroxyphenyl methyl sulfone in alcoholic sodium ethoxide, the primary band maximum undergoes a further displacement of 30 mμ toward the visible region of the spectrum (Fig. 1). This result may be compared with the 35 mμ displacement in the same direction which has been reported[7] to accompany the transformation of the *p*-hydroxybenzoate anion into the corresponding doubly charged anion. It seems reasonable to assume that the factors contributing to the ultraviolet absorption are similar in both cases; namely, resonance interactions between electron-releasing ($+M$) and electron-withdrawing ($-M$) substituents ($-\underset{\cdot\cdot}{\ddot{O}}:\ominus$ and $-SO_2CH_3$ or $-COO\ominus$, respectively).

As would be expected in view of the similar electron-releasing abilities of $-\ddot{N}H_2$ and $-\underset{\cdot\cdot}{\ddot{O}}:\ominus$,[9] the spectrum of *p*-aminophenyl methyl sulfone (Fig. 2) in neutral solution is almost identical with that of *p*-hydroxyphenyl methyl sulfone (Fig. 1) in alkaline solution. Also in accordance with prediction,[9] the $-NH_3\oplus$ group, which certainly promotes a strong inductive ($-I$) effect but is considered to be incapable of participating in a resonance ($-M$) effect, brings about no significant change in the spectrum of the parent sulfone when substituted

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[3] Fehnel and Carmack, THIS JOURNAL, **71**, 231 (1949).

[4] Koch, *J. Chem. Soc.*, 408 (1949).

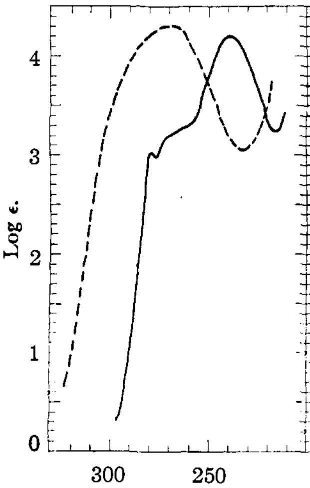
[5] Kumler and Strait, THIS JOURNAL, **65**, 2349 (1943).

[6] For a recent review article on the relationships between absorption spectra and constitution of organic molecules, see Ferguson, *Chem. Revs.*, **43**, 385 (1948).

[7] Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947); **71**, 2414 (1949).

[8] The nomenclature is that employed by Doub and Vandenbelt, ref. 7.

[9] *Cf.* Fehnel and Carmack, THIS JOURNAL, **71**, 2889 (1949), and references given there.



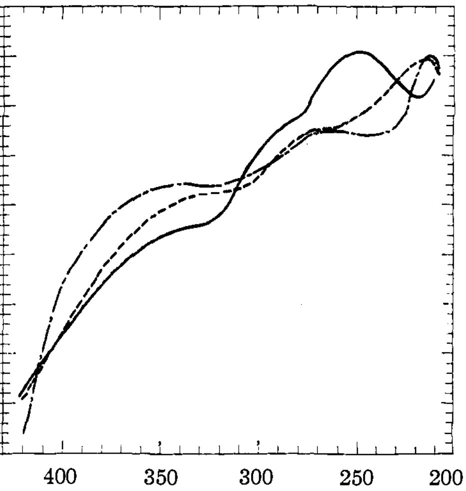


Fig. 1. Fig. 2. Fig. 3.

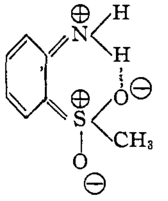
Fig. 1.—Absorption spectra of p-$\mathrm{HOC_6H_4SO_2CH_3}$ in EtOH, —, and in 0.01 N NaOEt, -----.

Fig. 2.—Absorption spectra of p-$\mathrm{NH_2C_6H_4SO_2CH_3}$ in EtOH, —, and in 2 N aq. HCl, -----; o-$\mathrm{NH_2C_6H_4SO_2CH_3}$ in EtOH, —·—·—, and in 2 N aq. HCl, — — —.

Fig. 3.—Absorption spectra of p-$\mathrm{NO_2C_6H_4SO_2CH_3}$, —; o-$\mathrm{NO_2C_6H_4SO_2CH_3}$, -----; 2,4,6-$\mathrm{(CH_3)_3C_6H_2NO_2}$, —·—·—; solvent, EtOH.

in the *para* position. Thus the spectrum of *p*-aminophenyl methyl sulfone in 2 N hydrochloric acid (Fig. 2) closely resembles that of phenyl methyl sulfone in ethanol.

The marked differences between the spectra of the *o*- and *p*-aminophenyl methyl sulfones (Fig. 2) are qualitatively similar to the characteristic differences which have been observed in the spectra of other pairs of *ortho* and *para* isomers,[10] and are probably to be attributed either to steric inhibition of resonance in the *ortho* compounds or to chelate ring formation by intramolecular hydrogen bonding. In this connection, it is interesting to compare the spectroscopic behavior of the *o*- and *p*-amino sulfones in acid media. As noted above, the spectrum of *p*-aminophenyl methyl sulfone reverts to that of phenyl methyl sulfone when the amine is dissolved in 2 N hydrochloric acid, indicating that the conversion of the amine into its conjugate acid is essentially complete under these conditions. The absorption spectrum of *o*-aminophenyl methyl sulfone in the same solvent, on the other hand, appears to be a combination of the spectra of the free base and its conjugate acid,[11] which implies that the *ortho* compound is a weaker base than its *para* isomer. Since the steric effect of the methylsulfonyl group in the *ortho* compound would be expected to *increase* rather than decrease the base strength relative to the *para* isomer,[12] we may, tentatively at least, attribute the observed effect to resonance contributions from structures such as I, in which the tendency of the aminophenyl chromophore to



I

assume a planar configuration[13] is augmented by intramolecular hydrogen bonding.[14]

In agreement with Doub and Vandenbelt's observations[7] on *p*-disubstituted benzene derivatives in which both substituents are electron-withdrawing groups (*e. g.*, *p*-dinitrobenzene and *p*-nitrobenzoic acid), *p*-nitrophenyl methyl sulfone (Fig. 3) exhibits a primary band maximum ($\lambda_{\max.}$ 248 mμ) at *shorter* wave length than in the spectrum of the parent monosubstituted compound having the longest wave length primary band (nitrobenzene, $\lambda_{\max.}$ 269 mμ). The even greater displacement of the primary band toward shorter wave lengths in the spectrum of *o*-nitrophenyl methyl sulfone ($\lambda_{\max.}$ 214 mμ) is clearly attributable to steric interference, by the methylsulfonyl group, with the coplanar configuration of the nitrophenyl

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[10] Compare, for example, the spectra of *o*- and *p*-hydroxyphenyl methyl sulfides [Fehnel and Carmack, ref. 9], *o*- and *p*-nitroanilines [Remington, THIS JOURNAL, **67**, 1838 (1945)], and *o*- and *p*-amino and hydroxy aldehydes, ketones, acids and esters [Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940)].

[11] We are making the not unreasonable assumption that the absorption spectrum of the *o*-methylsulfonylanilinium ion, like that of the corresponding *p*-anilinium ion, is similar to that of phenyl methyl sulfone.

[12] See, for example, the discussion by Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 177, 189–190.

[13] *Cf.* Klevens and Platt, THIS JOURNAL, **71**, 1714 (1949).

[14] It does not necessarily follow that the entire chelate ring must be coplanar. Other evidence indicates that the oxygen atoms and the methyl carbon atom are not in the plane of the remainder of the molecule; *vide infra*.

chromophore. This conclusion is supported by the close resemblance between the spectrum of *o*-nitrophenyl methyl sulfone and that of nitromesitylene ($\lambda_{max.}$ 214 mμ), in which conjugation between the benzene ring and the nitro group appears to be almost completely inhibited by the bulky *ortho* substituents.[15]

Steric Effects in *o*-Methyl Phenyl Sulfones.—The usual effect of a *p*-methyl substituent on the absorption spectrum of the parent monosubstituted benzene derivative is to bring about a bathochromic displacement of the primary band accompanied by a slight increase in intensity.[7,13,16] Among the phenyl sulfones, this effect is apparent in the shift of the primary absorption maximum from 217 mμ (log ϵ 3.83) in the spectrum of phenyl methyl sulfone to 225 mμ (log ϵ 4.07) in the spectrum of *p*-tolyl methyl sulfone (Fig. 4). Among other classes of compounds, the substitution of additional methyl groups in the *ortho* positions, however, generally results in a regression of both the primary and secondary bands[17] to shorter wave lengths and lower intensities because of steric inhibition of resonance in the principal chromophore.[13,15,18] The characteristic effects are, for example, clearly observed in the spectra of 2,4,6-trimethylbenzoic acid and its anion,[19] showing that the carboxyl group, which we have considered to be very similar to the sulfonyl group in its electrical properties, is susceptible to the usual steric influences. It is somewhat surprising, therefore, to observe that the presence of the *o*-methyl substituents in mesityl methyl sulfone (Fig. 4) and mesityl sulfone (Fig. 5) not only fails to bring about the usual hypsochromic displacement but actually produces a marked shift toward the visible region of the spectrum. This result would be anticipated only if the *o*-methyl substituents failed to interfere sterically with the postulated resonance interaction between the sulfonyl group and the benzene ring, while contributing, along with the *p*-methyl group, to the stabilization of the excited polar states responsible for the absorption.

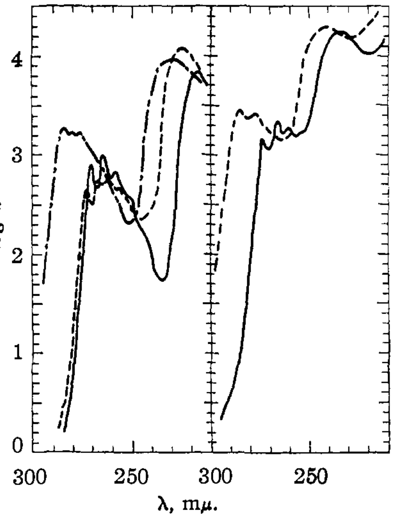


Fig. 4. Fig. 5.

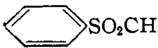
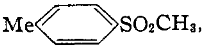
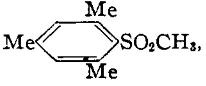
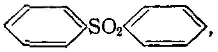
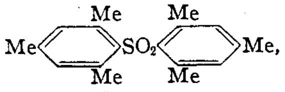
Fig. 4.—Absorption spectra of  SO_2CH_3, ——;  $MeC_6H_4SO_2CH_3$, - - - - -;  $Me_3C_6H_2SO_2CH_3$, —·—·—; solvent, EtOH.

Fig. 5.—Absorption spectra of  $(C_6H_5)_2SO_2$, —;  $(Me_3C_6H_2)_2SO_2$, —·—·—; solvent, EtOH.

Since the interference radius of the sulfone group is such that a coplanar configuration of the S, O and aromatic C atoms in the *o*-methyl phenyl sulfones would represent an even more highly strained condition than in the case of the corresponding nitro and amino compounds, we are led to conclude that the sulfur atom (in the sulfone function, at least) is capable of participating to an abnormally high degree in resonance within a non-planar system.[20] Theoretical justification for this conclusion may be derived from a consideration of the stereochemistry of 5-covalent systems. The formation of five covalent bonds by dsp^3 hybridization is considered to lead to a trigonal bipyramidal arrangement of groups about the central atom (Figs. 6-1 and 6-2).[21] If, however, the five pairs of electrons in the valence shell of the central atom are involved in bond-formation with only four other atoms (*i. e.*, if two of the bonds constitute a double bond directed toward a single atom, as FO in Fig. 6-4), then the attached atoms might be expected to assume either a square planar or *an approximately tetrahedral configuration* about the central atom (Fig. 6-3), depending upon whether the double bond is considered to derive from bonds directed toward two equatorial vertices (OB, OC, OD) or toward one equatorial vertex (*e. g.*, OD) and one of the pyramidal apices (*e. g.*, OA). It is probably significant to note that there are twice as many opportunities for double-bond formation by the latter process as by the former. In any event, existing physical data[22] on sulfones have been interpreted as evi-

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[15] Brown and Reagan, THIS JOURNAL, **69**, 1032 (1947).

[16] (a) Price, *Chem. Rev.*, **41**, 257 (1947); (b) Matsen, Robertson and Chuoke, *ibid.*, **41**, 273 (1947); (c) Platt and Klevens, *ibid.*, **41**, 301 (1947).

[17] These are the C and D bands, respectively, referred to by Klevens and Platt, ref. 13.

[18] Remington, ref. in footnote 10.

[19] Fehnel, THIS JOURNAL, **72**, 1404 (1950).

[20] *Cf.* Koch, ref. 4, cited earlier by Leonard and Sutton, THIS JOURNAL, **70**, 1564 (1948); see also Fehnel and Carmack, ref. 9.

[21] (a) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1944, pp. 102–103; (b) Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (c) Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 1945, p. 86; (d) Duffy, *J. Chem. Phys.*, **17**, 196 (1949).

[22] Maclean and Adams, THIS JOURNAL, **55**, 4683 (1933); Lüttringhaus and Buchholz, *Ber.*, **72B**, 2057 (1939); Lister and Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939); Toussaint, *Bull. soc. chim. Belg.*, **54**, 319 (1945); Leonard and Sutton, ref. in footnote 20.

dence for a "readily deformable, approximately tetrahedral arrangement of valence bonds"[23] about the sulfur atom. It seems probable, therefore, that when the sulfone function is attached to electron-releasing groups the observed tetrahedral configuration may involve contributions both from the dsp^3 hybridization of pentacovalent sulfur bond orbitals and from the conventional sp^3 hybridization of tetracovalent sulfur orbitals.[24]

These considerations indicate that non-coplanarity of atoms or groups about sulfur does not necessarily preclude the possibility of extensive resonance interaction between the sulfur-containing function and attached unsaturated functions. The often repeated statement that resonance in conjugated systems implies coplanarity of all the conjugated atoms actually applies only to first-row elements, where the valence-bond geometry is determined exclusively by s and p orbitals. Thus it follows from the tetrahedral (sp^3) configuration of the four valence-bond orbitals about carbon that utilization of two of these orbitals for double-bond formation should lead to a planar triangular arrangement of the three attached atoms about the central carbon atom, and in the various resonance structures which may be constructed for a conjugated system involving only first-row elements all of the conjugated atoms must necessarily lie in the same plane. As has been demonstrated above, no such limitation should apply to functions derived from the heavier elements (*e. g.*, sulfur in the sulfone function) where the utilization of *d* orbitals might permit the formation of double bonds between the central atom and one or more of the mutually non-coplanar atoms attached to it.[25]

An alternative and perhaps more fundamental approach to this problem of resonance in non-coplanar systems is provided by some recent observations of Klevens and Platt[13] on the spectra of substituted anilines. These investigators have shown that in the N,N-dimethylanilines the $-N(CH_3)_2$ group twists with relation to the benzene ring as groups of progressively larger radii are substituted in the ortho position and that the changes in the spectra are quantitatively related to the angle of twist. The twist is considered to cause a proportionate loss of double-bond character in the nitrogen–phenyl bond as a result of the diminished coupling between the π-electron orbitals when the parallel orientation of these orbitals is destroyed. The significant fact for the purposes of the present discussion is that the π-orbital interaction (*i. e.*, the conjugative effect) does not vanish until the angle of twist reaches 90°, that is, until the π-orbital axes are oriented at right angles to each other. In view of the many directional possibilities for π-bond formation by sulfur when the d-orbitals are involved, it seems likely that an appreciable amount of π-orbital interaction might occur across the sulfur–phenyl bond in spite of the tetrahedral arrangement of the σ valence bonds. Furthermore, the proximity of the *o*-methyl carbon atoms and the sulfone oxygen atoms in the compact mesityl sulfone and mesityl methyl sulfone molecules might be considered to favor a certain amount of hydrogen bonding between these atoms, thereby promoting the hyperconjugative resonance which should further stabilize the excited polar states in these molecules. The unusual features in the spectra of the *o*-methyl phenyl sulfones can thus be accounted for in terms of current concepts of molecular structure.

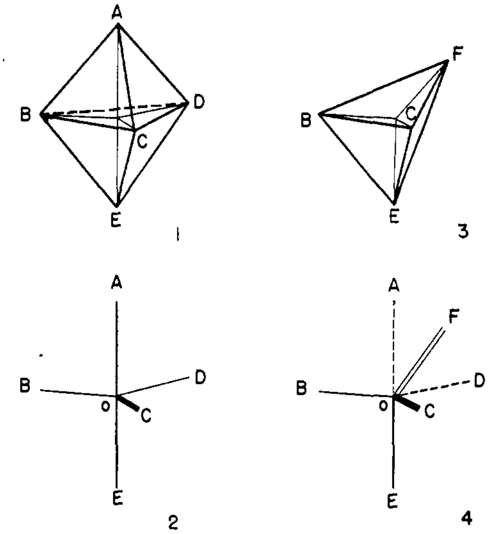

Fig. 6.

Experimental

The ultraviolet absorption measurements were made as described in a previous paper in this se-

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[23] Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 659.

[24] The octahedral symmetry which would result from the d^{2}sp^3 hybridization in 6-covalent sulfur atoms may be treated in an entirely analogous manner by constructing two double bonds from four of the octahedrally directed single bonds. In this case, also, most of the possible bond combinations lead to an approximately tetrahedral configuration of four groups about the central atom. It may be added that the usual distortion of all the bond angles attendant on multiple bond formation is to be expected in these cases and that it should operate in such a way as to produce a more nearly *regular tetrahedral* configuration than is indicated, for example, in Fig. 6-3. The relative positions of the central atom and the four atoms attached to it might well be approximately the same, therefore, in all of the possible bond states, a condition which must be fulfilled to meet the requirements of resonance theory. A mathematical treatment of the problem of directed valence employing the methods of group theory has been given by Kimball (ref. 21b), who considers that resonance between single- and double-bonded configurations may occur in certain tetrahedral 4-coördinate systems, including the $SO_4^=$ ion. See also a recent discussion of sulfur valence angles by Mathieson and Robertson, *J. Chem. Soc.*, 724 (1949).

[25] This concept might afford an adequate explanation of the seemingly anomalous geometry of several compounds discussed by Pauling (ref. 21a, especially pp. 228–235 and 250–253). Thus silicon tetrafluoride and nickel tetracarbonyl both appear to involve contributions from double-bonded structures utilizing d orbitals of the central atom, yet both retain a tetrahedral configuration. Pauling concludes that "[the single-bonded structures] seem to play a determinative part with respect to the stereochemical properties of the central atom"[21a]; *cf.* Wells, *J. Chem. Soc.*, 55 (1949).

ries.[26] The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED PHENYL SULFONES

Compound	Source[a]	Solvent[b]	Maxima[c] λ (mμ)	Maxima[c] log ε
Phenyl methyl sulfone	1	EtOH	271	2.91
			264	2.99
			258	2.82
			(253)	2.58
			217	3.83
p-Tolyl methyl sulfone	2	EtOH	273	2.66
			267	2.73
			262	2.75
			257	2.65
			225	4.07
Mesityl methyl sulfone	3	EtOH	285	3.26
			280	3.21
			277	3.23
			230	3.95
p-Hydroxyphenyl methyl sulfone	3	EtOH	279	3.03
			(268)	3.22
			239	4.20
p-Hydroxyphenyl methyl sulfone	3	NaOEt	269	4.31
p-Aminophenyl methyl sulfone	3	EtOH	269	4.30
			213	4.01
p-Aminophenyl methyl sulfone	3	HCl	270	2.99
			263	3.03
			258	2.91
			216	3.97
o-Aminophenyl methyl sulfone	3	EtOH	312	3.62
			245	3.95
o-Aminophenyl methyl sulfone	3	HCl	305	2.47
			272	3.16
			(264)	3.27
			251	3.36
			209	3.97
p-Nitrophenyl methyl sulfone	3	EtOH	(330)	3.79
			(282)	3.36
			248	4.05
o-Nitrophenyl methyl sulfone	3	EtOH	(318)	2.65
			268	3.26
			214	3.99
Phenyl sulfone[d]	1	EtOH	274	3.16
			266	3.33
			260	3.25
			(254)	3.21
			235	4.24
Mesityl sulfone	4	EtOH	286	3.44
			277	3.41
			241	4.28
Nitromesitylene[e]	5	EtOH	335	2.71
			260	3.28
			214	4.01

[a] Source references: (1) Fehnel and Carmack, ref. in footnote 3; (2) Gilman and Beaber, THIS JOURNAL, 47, 1450 (1925); (3) see section on "Preparation of Compounds"; (4) Maclean and Adams, ref. in footnote 22; (5) Powell and Johnson, "Organic Syntheses," Coll. Vol. II, 449 (1943). [b] EtOH designates absolute ethanol; NaOEt designates 0.01 *N* sodium ethoxide prepared by dissolving sodium in absolute ethanol; HCl designates 2 *N* aqueous hydrochloric acid. [c] The wave lengths in parentheses refer to inflection points. [d] *Cf.* Koch, ref. 4. [e] Included for comparison; *cf.* Brown and Reagan, ref. 15.

Preparation of Compounds.—All of the compounds studied were purified by two or more recrystallizations immediately before determination of the spectra. Phenyl methyl sulfone, *p*-tolyl methyl sulfone, phenyl sulfone, mesityl sulfone and nitromesitylene were prepared by procedures previously described in the literature, references to which are included in Table I.

p-Hydroxyphenyl methyl sulfone,[27] m.p. 91–92° (recrystallized from benzene); *p*-nitrophenyl methyl sulfone,[28] m.p. 139–140° (from ethanol); and *o*-nitrophenyl methyl sulfone,[29] m.p. 104–105° (from aqueous ethanol), were prepared by treatment of the corresponding sulfides[9] with excess 30% hydrogen peroxide in acetic acid solution. *p*-Aminophenyl methyl sulfone,[28] m.p. 133–134° (from benzene), and *o*-aminophenyl methyl sulfone, m.p. 82–83° (from aqueous ethanol),[30] were obtained from the corresponding nitrophenyl sulfones by reduction with stannous chloride and dry hydrogen chloride in glacial acetic acid.[31]

Mesityl methyl sulfone was prepared by treating a cold solution of 14.3 g. (0.086 mole) of mesityl methyl sulfide[9] in 90 ml. of glacial acetic acid with 22.6 ml. (0.20 mole) of 30% hydrogen peroxide, distilling off most of the solvent, and diluting the residual oil with water. The resultant precipitate was collected, washed with water, and dried *in vacuo* to afford 15.5 g. (91%) of crude product melting at 129–132° (cor.). Recrystallization of this material from aqueous ethanol (Norit) gave colorless leaflets, m.p. 131–132° (cor.).

Anal.[32] Calcd. for $C_{10}H_{14}O_2S$: C, 60.56; H, 7.12. Found: C, 60.56; H, 7.27.

Summary

The ultraviolet absorption spectra of a number of *o*- and *p*-substituted phenyl sulfones have been determined. The preparation of mesityl methyl sulfone is described.

Strong bathochromic displacements relative to the parent monosubstituted compounds are observed with *p*-hydroxy- and *p*-aminophenyl methyl sulfones, and in general the spectral characteristics of these compounds in various media are found to be similar to those of the corresponding substituted benzoic acids. These results are considered to support the view that the sulfone function, like the carboxylate function, participates in conjugative interaction with the aromatic nucleus. In agreement with previous observations on other *p*-disubstituted benzene derivatives in which both substituents are of the electron-withdrawing (−*M*) type, *p*-nitrophenyl methyl sulfone exhibits a primary band maximum at shorter wave length than does the parent monosubstituted compound having the longest wave length primary band. The spectra of *o*-amino- and *o*-nitrophenyl methyl sulfones give evidence of steric influence by the methylsulfonyl group on the resonance interaction between the

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[26] Fehnel and Carmack, THIS JOURNAL, 71, 84 (1949).

[27] Zincke and Ebel, *Ber.*, 47, 1106 (1914).

[28] Waldron and Reid, THIS JOURNAL, 45, 2399 (1923).

[29] Foster and Reid, *ibid.*, 46, 1936 (1924).

[30] This compound was previously reported (ref. 29) as an oil.

[31] *Cf.* Amstutz, Fehnel and Woods, THIS JOURNAL, 69, 1922 (1947).

[32] Semi-microanalysis performed by Mrs. Sarah M. Woods.

amino and nitro groups and the benzene ring.

The usual resonance inhibition by *o*-methyl substituents is not observed with the mesityl sulfones, the spectra of which are shifted toward the visible relative to the phenyl and *p*-tolyl sulfones. On the basis of these observations and of a consideration of the geometry of penta- and hexacovalent systems, it is concluded that a coplanar configuration of unsaturated atoms or groups about sulfur is not a prerequisite for resonance involving the sulfone function.

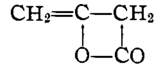
SWARTHMORE, PA. RECEIVED AUGUST 25, 1949

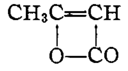
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of the Acidic Dimer of Methylketene

BY R. B. WOODWARD AND GILBERT SMALL, JR.

The extraordinary chemical behavior of the ketene dimers has lent exceptional interest to that class of substances, and the controversy which has raged for decades over the structures of the compounds is without parallel in the study of small molecules. Although many expressions have been considered[1] for the dimer from ketene itself the evidence now available is conclusive in favor of the view that diketene is one or the other, or a mixture, of the β-lactones (I) and (II). It is clear that (I) can be formed by the spontaneous *asymmetrical* dimerization of ketene, and the possibility of prototropic isomerization of (I) to (II) needs no further comment here. Dialkyl ketenes (III), on the other hand, dimerize *symmetrically* to tetraalkylcyclobutanediones (IV).[2]


I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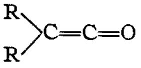
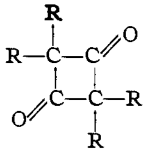
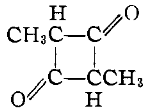

III

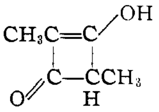

IV

The circumstances obtaining in the intermediate case of the aldoketenes have not hitherto been defined precisely. Methylketene (V) may be considered the prototype of this class. Two dimers of the aldoketene have been reported: (i) a *liquid* dimer, whose physical and chemical properties mirror those of diketene,[3a,b,c] and (ii) a *crystalline*, acidic dimer, m. p. 140°.[3a,b] It has been claimed that the liquid dimer is convertible into the acidic isomer by the action of bases, and the suggestion has been made that the change is that of a diketone (VI) into the corresponding enol (VII).[4] Other investigators have tentatively accepted the formulation of the acid dimer as (VII), while assuming that the liquid dimer was correctly represented by a β-lactone structure analogous to that of diketene.[5] No unequivocal structure proof has been brought forward for either of the dimers. Although (VI) is a plausible product of the symmetrical dimerization of methylketene, and (VII) might be expected to exhibit properties consonant with those of the acidic dimer, structural features are present which are sufficiently unusual as to justify considerable skepticism in the absence of definitive evidence of the correctness of the expressions. It is true that a synthesis of the acidic dimer from dimethyl α,α′-dimethylacetonedicarboxylate (VIII), through an intermediate of the presumed structure (IX), has been adduced in support of the structure (VII),[4b,6] but it will be seen in the sequel that this work, while of great value in providing a ready source of the dimer, whose preparation through methylketene is tedi-

$CH_3CH{=}C{=}O$

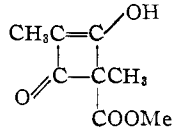
V


VI


VII


$MeOOC\overset{\displaystyle CH_3}{\overset{|}{C}}HCO\overset{\displaystyle CH_3}{\overset{|}{C}}HCOOMe$

VIII


IX

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[1] Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); Staudinger and Bereza, *Ber.*, **42**, 4908 (1909); Chick and Wilsmore, *J. Chem. Soc.*, **97**, 1978 (1910); Hurd, Sweet and Thomas, THIS JOURNAL, **55**, 337 (1933); Angus, Leckie, Le Fevre and Wassermann, *J. Chem. Soc.*, 1751 (1935); Hurd and Williams, THIS JOURNAL, **58**, 962 (1936); Hurd and Roe, *ibid.*, **61**, 3355 (1939); Boese, *Ind. Eng. Chem.*, **32**, 16 (1940); Hurd and Abernethy, THIS JOURNAL, **62**, 1147 (1940); Hurd, Calvin and Magel, *ibid.*, **63**, 2174 (1941); Oesper and Smyth, *ibid.*, **64**, 768 (1942); Hurdis and Smyth, *ibid.*, **65**, 94 (1943); Rice and Roberts, *ibid.*, **65**, 1677 (1943); Taufen and Murray, *ibid.*, **67**, 754 (1945); Whiffen and Thompson, *J. Chem. Soc.*, 1005 (1946); Bauer, Bregman and Wrightson, Abstracts April, 1946, Meeting, Am. Chem. Soc., p. 15p; Fitzpatrick, THIS JOURNAL, **69**, 2236 (1947); Blomquist and Baldwin, *ibid.*, **70**, 29 (1948); Miller and Koch, *ibid.*, **70**, 1890 (1948).

[2] Wedekind and Weisswange, *Ber.*, **39**, 1631 (1906); Staudinger, *ibid.*, **44**, 521 (1911); Miller, Dissertation, Cornell University, 1937; Hammick, Hampson and Jenkins, *Nature*, **136**, 990 (1935); Jenkins, *J. Chem. Soc.*, 862 (1936).

[3] Staudinger, *Ber.*, **41**, 906 (1908); **44**, 533 (1911); Sauer, THIS JOURNAL, **69**, 2444 (1947).

[4] Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 42; Staudinger, *Ber.*, **53**, 1085 (1920).

[5] Hill, Dissertation, Cornell University, 1941; Roberts, Armstrong, Trimble and Burg, THIS JOURNAL, **71**, 843 (1949).

[6] Schroeter and Stassen, *Ber.*, **40**, 1604 (1907); Schroeter, *ibid.*, **49**, 2697 (1916); **59**, 973 (1926).