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Cumulative Influence of Conjugated Substituents on the π -System Properties of Aromatic Hydrocarbons. II.¹ The Methoxybenzenes

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The electronic spectra and molecular complex spectra of the methoxybenzenes are reported and compared to Hückel molecular orbital calculations. Some related work with 1,2-dioxymethylenebenzene and derivatives is also reported.

Introduction

It is well established that a number of the measurable physical properties of unsaturated organic molecules, particularly aromatic hydrocarbons, are best explained in terms of the energies and distributions of electrons in delocalized molecular orbitals.² When series of similar unsaturated compounds are investigated, many of these properties, such as electronic and magnetic spectra and electrochemical potentials, can be correlated to the properties predicted by the simple Hückel molecular orbital (HMO)² theory. This theory is regarded as "simple" because it neglects all interelectronic interactions, even among the electrons in the delocalized π -system itself. The omission of such interelectronic interactions is serious and frequently not justifiable³; nevertheless with due caution many useful correlations with the HMO theory have been obtained.²

For the most part, the studies that have been made of the relationship of the HMO theory to physical properties of molecules have confined themselves either to aromatic hydrocarbon molecules, or heteroaromatic molecules, or to aromatic or heteroaromatic groups linked by conjugated open chains. Very few systematic investigations of aromatic molecules containing some of the more common substituents have been reported. Those investigations that have been made have generally been for aromatic molecules substituted with a single hetero group.⁴ The only extensive studies of multiply-substituted aromatics have been those made on the readily available methylbenzenes. Unfortunately, while the compounds are available, the interaction of the methyl group with the benzene ring is weak, and its nature has proved complex and remains controversial.⁵ Other, more strongly interacting substituents on an aromatic nucleus, such as methoxy-, methylthio-, dimethylamino-, cyano-, etc., may extend an aromatic π -system in a regular way to give predictable properties and could prove more amenable to simple theoretical treatment. Thus, our preliminary work¹ indicated that an energy level property of the methoxybenzenes, their relative charge-transfer absorption maxima with a fixed acceptor (tetracyanoethylene), can be satisfactorily described by the HMO picture.

Since multiple substitution of aromatic molecules can result in unusual physical properties,⁶ it is of interest to

see to what extent the physical properties of such highly substituted compounds are predicted by the HMO method. The present series of papers will report on our investigation of the electronic and magnetic spectra, electrochemical potentials, and other physical properties of multiply-substituted unsaturated compounds, and compare these properties to those predicted by HMO theory.

In this paper we will deal with an investigation of the π -system properties of the benzene nucleus substituted only by ethereal oxygen, as represented by either the methoxy or 1,2-dioxymethylene groups. In our model of these molecules the π -system is regarded as extended from the benzene ring to a filled "nonbonding" orbital of oxygen. No attempt is made to define the manner in which electrons in the oxygen orbitals exchange with the benzene π -system, as this is unnecessary for the HMO treatment.⁷ No interaction of the π -system with the terminal methyl or methylene groups is explicitly considered, although implicitly the effect of the alkyl group on the oxygen coulomb integral is included in the selection of the latter; MO calculations made on molecular orbital systems containing different types of atoms and bonds require assignments of coulomb and resonance integrals. In the usual Hückel treatment the assignments are made relative to a standard coulomb integral (α_c) and resonance integral (β_{cc}) of benzene, and take the form of eq. 1 and 2 where α_x and β_{cx} are

$$\alpha_x = \alpha_c + h\beta_{cc} \quad (1)$$

$$\beta_{cx} = k\beta_{cc} \quad (2)$$

the new coulomb and resonance integrals, and h and k are parameters characteristic of the new atoms and bonds. For the interaction of ethereal oxygen with the benzene ring, we have used $h = 2.0$ and $k = 0.8$, as suggested by Streitwieser.² With the hetero parameters assigned, the secular determinants were written in the usual manner.² Solution of the determinants was made by factoring, which employed the symmetry properties of the molecules,⁸ followed by solution of the residual determinants by an iterative procedure on a Burroughs 205 computer.

Results and Discussion

Charge-Transfer Spectra.—The charge-transfer spectra of the methoxybenzenes with tetracyanoethylene have been reported elsewhere.¹ In Table I, we report the longest wave length charge-transfer absorption bands of the methoxybenzenes with the π -acceptors 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, *p*-chloranil,

(6) N,N,N',N'-Tetramethyl-*p*-phenylenediamine is a simple substituted benzene derivative which is a strong reduction agent [L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943)]. An unusually powerful organic oxidizing agent, cyanil (tetracyano-*p*-benzoquinone), can also be regarded as a substituted benzene molecule [K. Wallenfels and G. Bachmann, *Angew. Chem.*, **73**, 142 (1961)].

(7) Reference 2, p. 98.

(8) C. G. Swain and W. R. Thorson, *J. Org. Chem.*, **24**, 1989 (1959); also ref. 2, Chapter 3.

(1) Part 1 in this series is considered to be A. Zweig, *J. Phys. Chem.*, **67**, 506 (1963).

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) For example, see R. L. Miller and P. G. Lykos, *Tetrahedron Letters*, **No. 11**, 493 (1962).

(4) For example, the series of papers by F. A. Matsen, *et al.*, *J. Am. Chem. Soc.*, **72**, 5260 (1950).

(5) A monograph recently published on this subject is M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962. Extensive molecular orbital treatments of methylbenzenes are reported by A. S. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959); S. Ehrenson, *J. Am. Chem. Soc.*, **84**, 2681 (1962).

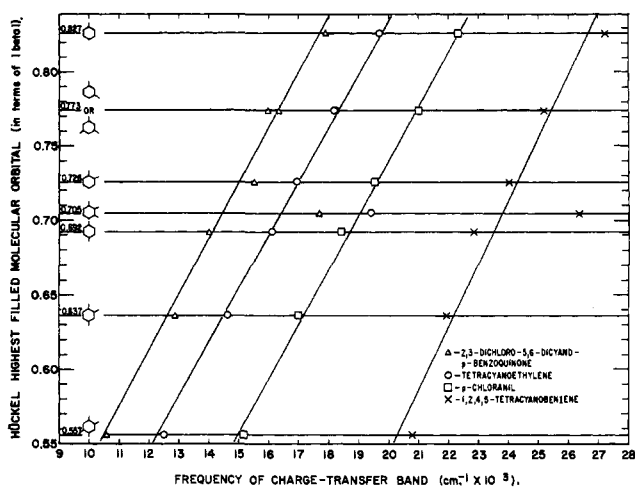


Fig. 1.—Plot of the transition energies of the first charge-transfer bands of some methoxybenzenes with various acceptors against the Hückel HFMO's.

and 1,2,4,5-tetracyanobenzene.⁹ The methoxybenzenes can be divided into two groups for theoretical purposes. The five methoxybenzenes with three or more adjacent methoxy groups are constrained for steric reasons from having all their methoxy groups in the plane of the benzene ring (steric inhibition of resonance), and are referred to here as the sterically constrained methoxybenzenes. The other seven compounds in the set are unconstrained, as they do not suffer this limitation on their configurations.¹⁰ As can be seen from Fig. 1, a plot of the energy of highest filled HMO's of the sterically unconstrained methoxybenzenes *vs.* their first charge-transfer absorption maxima with all four acceptors give nearly parallel lines, as determined by the least-squares method. It has been shown¹¹ that the slope of these lines with different acceptors should all be the same and equal to β since the difference in ground state energies may be neglected, and the only variable is the energy of the unfilled acceptor level. The values of the slope obtained from Fig. 1 are 3.28, 3.39, 3.35, and 3.28 e.v. for the methoxybenzene complexes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, tetracyanoethylene, *p*-chloranil, and 1,2,4,5-tetracyanobenzene, respectively. These compare with 3.00, 3.06, and 3.12 e.v. for the slopes of the charge-transfer complexes of *sym*-trinitrobenzene,¹¹ tetracyanoethylene,¹² and 2,4,7-trinitro-9-fluorenone¹³ with aromatic hydrocarbons.

Although all four acceptors gave reasonably sharp charge-transfer spectra with most of the methoxybenzenes (all reported measurements are ± 5 –10 μ), several combinations could not be measured. These were either because the charge-transfer band coincided with an absorption band of the donor or acceptor, or because the charge-transfer band was too broad and diffuse. Notable among the latter were the complexes of 1,2,3,4-tetramethoxybenzene. All of these complexes absorbed from 350 to 800 μ , without a definite maximum. Conformational instability may be a cause of this behavior. Of those acceptors investigated, tetracyanoethylene was most satisfactory for charge-transfer

(9) The acceptor properties of 1,2,4,5-tetracyanobenzene are reported in an accompanying paper: A. Zweig, J. E. Lehnsen, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **85**, 3937 (1963).

(10) Evidence from electric dipole moment measurements has indicated that an unhindered aryl methoxy group at room temperature spends most, but not all, of its time in the plane of the aromatic ring: G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 238.

(11) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

(12) M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962).

(13) A. R. Lepley, *ibid.*, **84**, 3577 (1962).

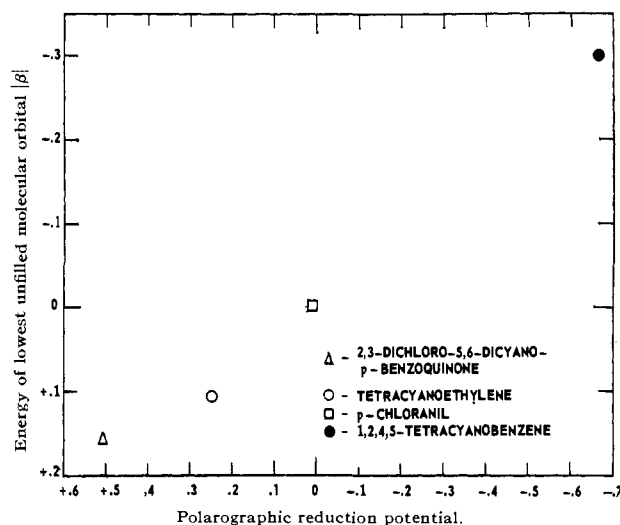


Fig. 2.—Plot of polarographic reduction potentials and energies of lowest unfilled orbitals of π -acceptors.

studies. Although 2,3-dichloro-5,6-dicyano-*p*-benzoquinone is a stronger π -acid than tetracyanoethylene, the latter almost invariably gave a more sharply defined charge-transfer maxima. It is therefore significant that the deviation from the least squares correlation lines in Fig. 1 is smallest for the complexes of tetracyanoethylene.

TABLE I
CHARGE-TRANSFER BANDS OF METHOXYBENZENE COMPLEXES^a

Donor compound	Acceptors		
	DiCICNBQ ^b frequency $\times 10^3$ cm. ⁻¹	<i>p</i> -Chloranil frequency $\times 10^3$ cm. ⁻¹	TCNB ^c frequency $\times 10^3$ cm. ⁻¹
Anisole	17.9	22.3 ^f	27.2
1,2-Dimethoxybenzene	15.5	19.5	24.0
1,3-Dimethoxybenzene	16.0	^d	^e
1,4-Dimethoxybenzene	14.0	18.4	22.8
1,2,3-Trimethoxybenzene	17.7	^d	26.4
1,2,4-Trimethoxybenzene	12.9	17.0	21.9
1,3,5-Trimethoxybenzene	16.3	21.0	25.2
1,2,3,4-Tetramethoxybenzene	^e	^e	^e
1,2,3,5-Tetramethoxybenzene	14.8	20.1	^e
1,2,4,5-Tetramethoxybenzene	10.6	15.2	20.8
Pentamethoxybenzene	14.2	^d	^e
Hexamethoxybenzene	17.3	^d	^e

^a All measured in methylene chloride unless otherwise noted.
^b 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. ^c 1,2,4,5-Tetracyanobenzene (*cf.* ref. 9). ^d Absorption could not be measured satisfactorily owing to interference by either donor or acceptor.
^e Very broad band; maximum could not be assigned $\pm 10 \mu$.
^f Solvent CCl₄, as reported by A. Kuboyama, *Nippon Kagaku Zasshi*, **81**, 558 (1960).

Comparison with Polarographic Data.—The intercept of the plotted lines in Fig. 1 with the *x*-axis gives the energy of the lowest unoccupied orbital of the acceptor in terms of the Hückel scale.¹¹ The energies of the lowest unoccupied orbitals of electron acceptors are also related to their polarographic half-wave reduction potentials.¹⁴ Peover¹⁵ has reported the polarographic half-wave reduction potentials of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, tetracyanoethylene, and *p*-chloranil in acetonitrile. We have obtained this information for 1,2,4,5-tetracyanobenzene.⁹

A plot of the experimentally obtained lowest unfilled orbital energy levels of these acceptors against the polarographic data is made in Fig. 2.

Second Charge-Transfer Maxima.—Because of their symmetry properties 1,3-dimethoxybenzene and 1,3,5-

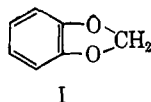
(14) Reference 2, Chapter 7.

(15) M. E. Peover, *Nature*, **191**, 702 (1961).

trimethoxybenzene have the same highest filled molecular orbital energies (the *sym*-trimethoxybenzene's highest filled orbital being degenerate). The charge-transfer absorption band maxima from the degenerate highest filled orbital of the *sym*-trisubstituted methoxybenzene were well defined; however, the 1,3-disubstituted compound gave broad charge-transfer maxima. This is seemingly due to overlapping of a second charge-transfer band which results from a transition from the second highest filled orbital of the donor to the lowest unfilled orbital of the acceptor. Orgel¹⁶ has shown that the separation of the double bands observed in the molecular complexes of methylbenzenes with *p*-chloranil correlate with the energy difference between the highest and second highest filled molecular orbitals of the donors. Merrifield and Phillips¹⁷ found similar agreement when they examined the tetracyanoethylene complexes of the methylbenzenes. Of the acceptors studied, tetracyanoethylene gave the most (7) well-defined second charge-transfer bands with the methoxybenzenes.¹ A plot of the *second* highest filled HMO's of the sterically unconstrained methoxybenzenes and their *second* charge-transfer bands with tetracyanoethylene is made in Fig. 3. The dotted line is a continuation of the correlation line of the first charge-transfer bands in Fig. 1. As expected, a good linear correlation of the second charge-transfer bands was *not* found. However, the trend is still discernible. For example, the second charge-transfer absorption bands of anisole and *p*-dimethoxybenzene are relatively close ($0.5 \times 10^3 \text{ cm.}^{-1}$ apart). Their next to highest filled HMO's would have them identical. The order of the energies of the second charge-transfer absorption bands (*p* > *o* > *m*) of the dimethoxybenzenes is also reproduced by the Hückel treatment. These transition energies are in opposite order from those of the first charge-transfer bands (*m* > *o* > *p*) and result in the *m*-isomer having the smallest separation between first and second charge-transfer transition energies of the three. For this reason, complexes of *m*-dimethoxybenzene exhibited broad charge-transfer absorption, and of those examined only the tetracyanoethylene complex was well enough resolved to measure the first and second absorption maxima.

Sterically Hindered Methoxybenzenes.—All methoxybenzenes containing hindered methoxy groups¹⁸ show π -basicity diminished from that predicted by their highest filled M.O.'s. Since the energy levels are sensitive to the choice of the resonance parameter *h*, one could diminish this parameter for the hindered groups to achieve the observed reduction in π -basicity.¹⁹ It seems reasonable to assume that methoxy groups flanked at both *o*-positions are the only hindered groups.²⁰ To test this hypothesis, compounds related to the methoxybenzenes could be examined.

The chemistry of 1,2-methylenedioxybenzene (I) is reported to be similar to that of 1,2-dimethoxybenzene.²¹



I

(16) L. E. Orgel, *J. Chem. Phys.*, **23**, 1352 (1955).

(17) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(18) The five methoxybenzenes with hindered methoxy groups are 1,2,3-trimethoxybenzene, 1,2,3,4-tetramethoxybenzene, 1,2,3,5-tetramethoxybenzene, penta-, and hexamethoxybenzene.

(19) A value of ~ 0.5 for the *h* parameter of the C-O bonds of the hindered methoxy groups, suggesting an out-of-plane angle of $\sim 38^\circ$ for the P_z orbital on the hindered oxygen, will bring the calculated highest or second highest filled MO's of 1,2,3-tri-, 1,2,3,5-tetra-, penta-, and hexamethoxybenzene in line with the energies of their charge-transfer complexes and the energies and HFMO's of the unhindered methoxybenzenes.

(20) Dipole moment studies have suggested this: K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 16 (1951).

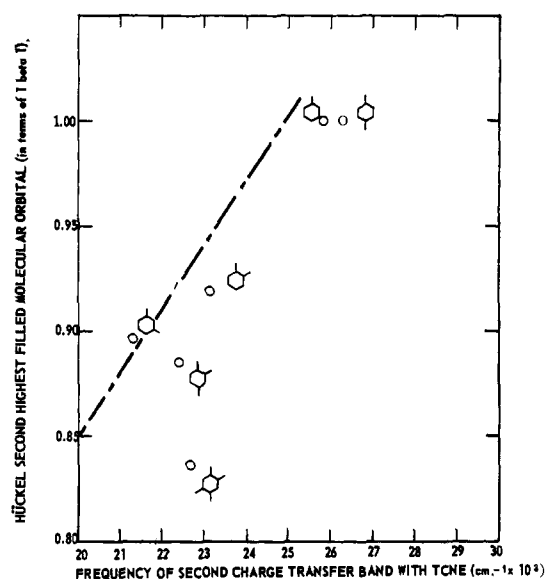
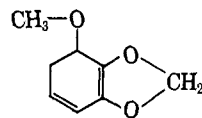


Fig. 3.—Plot of the transition energies of the second charge-transfer bands of some methoxybenzenes with tetracyanoethylene against the next to highest filled MO's.

The comparative π -basicity in molecular complexes of these two materials have not, however, been previously investigated. Table II reports the charge-transfer maxima obtained from these two aromatic diethers with four different acceptors. Within the accuracy of the charge-transfer absorption maxima measurements, the results indicate that both donors have nearly identical π -basicities. These results led us to examine the donor ability of 1-methoxy-2,3-methylenedioxybenzene (II).



II

It can be seen from Fig. 1 that the charge-transfer maxima of 1,2,3-trimethoxybenzene occur at frequencies $3 \times 10^3 \text{ cm.}^{-1}$ higher than predicted by the MO calculations. If steric inhibition of resonance of the ethereal oxygen at the 2-position is responsible for this decreased donor ability, then fixing the stereochemistry of the 2-oxygen to methylene bond in the plane of the ring, by means of the methylenedioxy bridge,²² could

TABLE II

CHARGE-TRANSFER BANDS OF 1,2-METHYLENEDIOXYBENZENE AND 1,2-DIMETHOXYBENZENE COMPLEXES IN METHYLENE CHLORIDE

Acceptor	Donor, $m\mu$	
	1,2-Methylene-dioxybenzene	1,2-Dimethoxybenzene
1,2,4,5-Tetracyanobenzene	407	410
<i>p</i> -Chloranil	500	512
Tetracyanoethylene	575	592
2,3-Dichloro-5,6-dicyano- <i>p</i> -benzoquinone	650	644

be expected to result in triether II having its charge-transfer maxima occur at the frequencies predicted for 1,2,3-trimethoxybenzene by the MO calculations. The complexes of II with the four acceptors in Fig. 1 were examined. The maxima of II with 1,2,4,5-tetracyano-

(21) R. T. Arnold and F. Bordwell, *J. Am. Chem. Soc.*, **64**, 2983 (1942). Evidence for the biogenical synthesis of the methylenedioxy group from *o*-methoxyphenols has been obtained: D. H. R. Barton, G. W. Kerby, and J. B. Taylor, *Proc. Chem. Soc.*, 340 (1962).

(22) The methylenedioxy bridge is in the plane of the benzene ring: W. J. Gensler, and C. M. Samour, *J. Org. Chem.*, **18**, 9 (1953).

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF THE METHOXYBENZENES IN CYCLOHEXANE AND THEIR HÜCKEL HFMO-LUMO INCREMENTS

Methoxybenzene	λ_{\max} , $m\mu$ (log ϵ)						HFMO-LUMO ($ \beta $)
	λ_1	λ_2	λ_3	λ_4	λ_5	λ_6	
Anisole	278 (3.34)	271 (3.32)	268 sh (3.14)	265 (3.17)	224 sh (3.80)	220 (3.90)	1.827
1,2-Di-	283 (3.28)	277 (3.40)	273 (3.38)	233 sh (3.69)	227 (3.87)	224 sh (3.86)	1.764
1,3-Di-	280 (3.34)	274 (3.34)	270 sh (3.25)	220 (3.86)			1.807
1,4-Di-	300 (3.41)	293 (3.50)	289 (3.51)	283 sh (3.40)	226 (3.98)		1.692
1,2,3-Tri-	275 sh (2.68)	267 (2.82)	222 sh (3.93)				1.800
1,2,4-Tri-	295 sh (3.35)	286 (3.54)	230 sh (3.84)	224 (3.86)			1.673
1,3,5-Tri-	270 sh (2.56)	265 (2.64)	223 (3.94)				1.881
1,2,3,4-Tetra-	283 (3.33)	223 sh (3.94)					1.726
1,2,3,5-Tetra-	277 (3.21)	225 sh (3.93)					1.719
1,2,4,5-Tetra-	292 (3.65)	230 (3.88)					1.630
Penta-	282 (3.36)	225 (3.97)					1.694
Hexa-	314 (1.64)	276 (2.74)					1.757

benzene and *p*-chloranil were too weak and diffuse to measure, and the complex with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone had a strong but broad charge-transfer absorption to which a maximum could not be assigned with reliability. Tetracyanoethylene, however, gave a sharp charge-transfer absorption maximum with II. This occurred at 530 $m\mu$ as compared to the 515 $m\mu$ maximum observed with 1,2,3-trimethoxybenzene. The expected 3×10^3 cm^{-1} frequency shift would have put the tetracyanoethylene charge-transfer maximum of II at ~ 610 $m\mu$. This result suggests that steric inhibition of resonance does not occur only at the 2-position of a 1,2,3-trisubstituted methoxybenzene, and that possibly a buttressing effect of substituents at the 2- and 3-positions can also interfere with the resonance of a substituent at the 1-position.

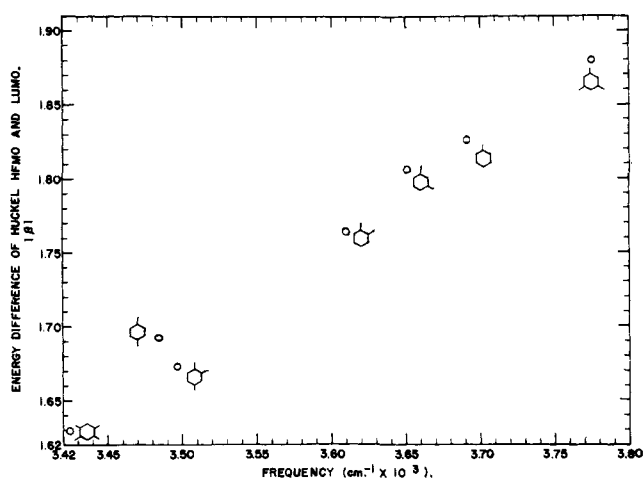


Fig. 4.—Plot of calculated energy differences against frequency of the strongest long wave length absorption of unhindered methoxybenzenes.

Electronic Spectra of the Methoxybenzenes.—It has been pointed out²³ that a theory based on a one-electron Hamiltonian, such as the Hückel theory, which does not take into account electronic interaction terms, will fail even to predict the correct order of the excited states. However, it has been known for over a decade²⁴ that the position of the first strong absorption band in the aromatic hydrocarbon series, Platt's 'L_a-band and Clar's p-band, can be correlated to the energy difference

(23) E. Heilbronner and J. N. Murrell, *J. Chem. Soc.*, 2611 (1962).

(24) M. J. S. Dewar, *ibid.*, 3532 (1952).

between the highest filled MO and lowest unfilled MO calculated by the Hückel method. As has been pointed out,²⁵ this and similar correlations probably means that there is a high degree of proportionality within a family of systems between the effects of such electronic interactions, and also of singlet-triplet splittings and the over-all transition energy.

Since the highest filled MO's of the unhindered methoxybenzenes correlate well with the Hückel approximation, we examined their ultraviolet spectra to see if the proportionality observed in the aromatic hydrocarbon family of compounds holds here. The spectral maxima and intensities of the methoxybenzenes in cyclohexane are reported in Table III, as are the calculated highest filled-lowest unfilled molecular orbital energy increments. A plot of the first strong absorption band against the MO increment is shown in Fig. 4. The proportionality of interelectronic interactions and of singlet-triplet splittings in this series thus also appears to be good. Although there is a choice of two almost equally strong long wave length maxima in anisole and 1,3-dimethoxybenzene, Fig. 4 suggests clearly which of these maxima involve the transition undergone by the other molecules.

Experimental

Materials.—The methoxybenzenes were obtained or prepared as previously described.¹ Redistillation or recrystallization of the commercial anisole, dimethoxybenzenes, and 1,2,4-trimethoxybenzene slightly raised the extinction coefficients of their absorption maxima, but did not affect the positions of the ultraviolet maxima or the positions of the charge-transfer maxima. *p*-Chloranil and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were purified by crystallization and sublimation before use. 1,2,4,5-Tetracyanobenzene was prepared and purified as described in the literature.²⁶ A commercial sample²⁷ of 1,2-dioxymethylenebenzene, distilled before use, was employed. 1-Methoxy-2,3-dioxymethylenebenzene was prepared by a modification²⁸ of the original synthesis.²⁹

Spectral Measurements.—Concentrated solutions of the methoxybenzenes and the various acceptors in spectral grade methylene chloride were mixed in equimolar proportions, then diluted if necessary to obtain the position of the absorption maxima. All spectral measurements were made on a Cary 14 spectrophotometer at 22°. Spectral grade cyclohexane was employed for the ultraviolet studies. Since only the charge-transfer maxima were relevant to this investigation, no attempt was made to measure equilibria and extinction coefficients for the complexes.

(25) Reference 2, p. 213.

(26) E. A. Lawton and D. D. McRitchie, *J. Org. Chem.*, **24**, 26 (1959).

(27) Obtained from Frinton Labs., Vineland, N. J.

(28) A. F. Wagner, E. Walton, A. N. Wilson, J. O. Rodin, F. W. Holly, N. G. Brink, and K. Folkers, *J. Am. Chem. Soc.*, **81**, 4983 (1959).

(29) K. N. Campbell, P. F. Hopper, and B. K. Campbell, *J. Org. Chem.*, **16**, 1736 (1951).