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THE ELECTRONIC EFFECT OF THE METHYL GROUP

PARTIAL RATE FACTORS FOR NITRATION OF THE XYLENES

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Abstract—The electronic effect of the Me group has been investigated using several different models within the PPP formalism. For Me substituted benzenes the optimum agreement between calculated and observed properties is obtained when both, inductive and hyperconjugative mesomeric effects of the substituent are included. The properties investigated are frequency shifts and changes in intensities of electronic transitions, changes in ionization potentials, changes in π charge distribution and positional and relative reactivities in electrophilic substitution. In the case of the latter the nitration (HNO_3/HOAC media) of the xylenes has been investigated over a wide temperature range, and competitive nitrations at 25° with benzene have been carried out to give partial rate factors.

INTRODUCTION

ANY theory of substituent effects should encompass a theoretical interpretation of as many experimentally observable quantities as possible. Thus within the Pariser–Parr–Pople pi electron framework[1,2] it should be possible to explain:

(a) Frequency shifts and changes in intensity of electronic transitions of aromatic compounds on substitution.

(b) Changes in orbital energies as evidenced by ionization potentials.

(c) Changes in charge distribution as evidenced by changes in ^{13}C and ^{1}H chemical shifts.

(d) Relative reactivities of substituted compounds towards a given electrophile, and positional selectivity within the aromatic nucleus.

A particularly suitable substituent for investigation is the Me group for which both field and sigma inductive effects are expected to be relatively unimportant. Previous workers have concentrated on either (a)[3–5] (b)[5,6] or (d)[7,8] with widely differing models for the electronic effect of a Me substituent, and for the particular property in question with a reasonable degree of success. However the situation is clearly unsatisfactory and a unified theoretical model of the electronic effect of a Me substituent which accommodates the experimental data (a)–(d) is required. In the particular case of Me substituted benzenes, there is a wealth of experimental data relating to (a)[9] and (b)[19] and hence these form a particularly useful set of compounds to develop a model of the electronic influence of a Me substituent capable of accommodating a wide variety of experimental data.

Dewar *et al.* have shown[11] that localization energies for electrophilic substitution, calculated within the framework of the PPP–SCF–MO method, correlate well with partial rate factors for nitration of aromatic hydrocarbons extending over a wide range of reactivities. It is therefore of considerable interest to see whether the theoretical treatment can be extended to Me substituted aromatic hydrocarbons. However there is a lack of experimental data. Partial rate factors for nitration in HNO_3/HOAc media are available for toluene[12] and the mono methylnaphthalenes,[13] and in the light of these results it is perhaps surprising that partial rate factors are not available for the xylenes. Olah's[12] investigations indicated that overall rates with respect to benzene, for nitration in HNO_3/HOAc media at 25°, were in excess of 1000 for both *p*- and *m*-xylenes. These results seem at a variance with those for toluene and the mono methyl naphthalenes. We have therefore reinvestigated the nitration, in HNO_3/HOAc media, of the xylenes over a wide temperature range to determine isomer distributions, and partial rate factors with respect to benzene. In this paper we present a theoretical interpretation of these experimental results using a model for the electronic effect of the Me group which gives in addition a unified interpretation of experimental results under the headings (a) to (c).

Frequency shifts and changes in intensity of electronic transitions of benzene on methyl substitution

Introduction. The intensity changes in the electronic spectrum of benzene have been treated by Craig and Doggett[3] assuming that the Me group has an inductive perturbation only. However such a model is basically incapable of accommodating the substantial frequency shifts induced by Me substitution in benzene. Within the framework of the localized orbital model Murrell *et al.* have shown[4] from Petruska's[9] analysis of spectral data, that a Me group exerts both a mesomeric and an inductive effect. Recently Clark and Emsley[14] have made calculations on substituted benzenes within the framework of the PPP–SCF–MO method treating the effect of the substituent as (i) purely inductive, (ii) mesomeric plus sigma inductive and (iii) mesomeric plus sigma and pi inductive. For the substituents investigated (F, Cl, OH, NH_2) the inclusion of mesomeric and both sigma and pi inductive effects (model iii) were required to give satisfactory agreement with experimentally determined quantities (a) and (c).

Method of calculation. The sigma and pi inductive effects have been incorporated into the standard PPP method as previously described[14] and the minimum of detail will be given here. The Me group may be considered as a pseudo atom situated at the position of the C atom, contributing two electrons to the pi system through hyperconjugation.[15] The first valence state ionization potential of this pseudo atom (I_μ) is taken as the first ionization potential of methane (13·12 eV).[16] The pseudo atomic orbital may be considered as a carbon $2p_z$ orbital and the two centre one electron integrals in the off diagonal elements of the F matrix (β's) calculated from the Wolfsberg Helmholtz formula[17] and the relevant overlap integrals. The one centre two electron repulsion integrals were taken to be those for carbon, valence state trtrtrπ.[18] The first term in the diagonal element of the F matrix, unmodified for the sigma and pi inductive effects is then equal to $H_{\mu\mu} = I_\mu + \gamma_{\mu\mu} = 24{\cdot}10$ eV. The inductive parameters using the nomenclature of Ref. 14 are $\alpha C(X)_\pi$ 0·47 eV, $\alpha C(X)_\sigma$ 0·0 eV, $\alpha X(C)_\pi$ 0·47 eV, $\alpha X(C)_\sigma$ 0·0 eV, and for the calculation of excited state and ground state properties the empirical $\beta_{CC} = -2371$ eV[19] and $-1{\cdot}75$ eV[20] respectively have been used. C–C bond lengths and angles were taken to be 1·39 Å and 120° respectively, and the pseudo orbital located 1·52 Å from the substituted C atoms. The calculations were carried out on the University of Newcastle's KDF 9 computer and configuration interaction between all singly excited states has been included.

Results and discussion. The electronic spectra of Me substituted benzenes have been analysed in detail by Petruska.[9] The results of calculations of the frequency shifts of the 2600 Å, 2050 Å and 1850 Å bands of benzene on Me substitution are shown in Table 1. The electronic effect of the Me group has been treated according to two

TABLE 1. FREQUENCY SHIFTS OF THE 2600 Å, 2050 Å AND 1850 Å BANDS OF BENZENE ON Me SUBSTITUTION

Position of Me groups	Model	Frequency shifts (cm^{-1})							
		2600 Å		2050 Å		1850 Å		$\Delta f_X/\Delta i_{\text{toluene}}$	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	iv	16		8		8		(1)	
	i	653		1339		1331		(1)	
	iii	782	610	1500	1400	1436	1400	(1)	1
1, 2	i	1194		2451		2629		1·31	
	iii	1379	920	2863	1900	2750	2100	1·33	1·1
1, 3	i	1129		2105		2710		0·93	
	iii	1194	1150	2218	2500	2865	2700	0·96	1·2
1, 4	i	1395		2508		1831		3·52	
	iii	1904	1390	2594	2900	1920	2500	3·28	3·40
1, 3, 5	i	1492		2637		3283		0	
	iii	1347	1520	2597	3300	3452	3800	0	0

TABLE 2. CHANGES IN IONIZATION POTENTIAL OF AROMATIC COMPOUNDS ON METHYL SUBSTITUTION

Compound	Model	$I_X - I_{\text{benzene}}$ (eV)	
		Calc.	Obs.[10]
Benzene		(0)	0
Toluene	iv	0·135	
	i	0·229	
	iii	0·379	0·425
o-Xylene	i	0·369	
	iii	0·616	0·690
m-Xylene	i	0·353	
	iii	0·574	0·685
p-Xylene	i	0·438	
	iii	0·720	0·800
Mesitylene	i	0·463	
	iii	0·642	0·975

models, (i) purely mesomeric, (iii) mesomeric plus sigma and pi inductive, and in the particular case of toluene, (iv) a purely inductive model). It is immediately obvious from the calculations on toluene that a purely inductive model for the electronic effect of the Me group is inadequate. Since the frequency shifts are dominated by the mesomeric effect of the Me substituent both models (i) and (iii) give similar results, which are in satisfactory agreement with experiment.

Also shown in Table 1 are the calculated and observed ratios of changes in oscillator strength of the 2600 Å band of benzene, with respect to toluene. Again both models (i) and (iii) are in good agreement with experiment.

Changes in orbital energies as evidenced by ionization potentials

Applying Koopman's theorem, the change in first ionization potential of benzene on Me substitution may be calculated directly from the relevant eigenvalues. The results are shown in Table 2.

It is evident that the pure inductive (iv) or mesomeric (i) models considerably underestimate the change in ionization potential, whilst the inductive mesomeric model (iii) brings the calculated and experimental values into reasonable agreement.

Changes in charge distribution as evidenced by changes in ^{13}C and ^{1}H chemical shifts

There are strong grounds for believing that the chemical shifts, relative to unsubstituted benzene of both ^{1}H and ^{13}C nuclei *para* to the substituent are directly proportional[21] to the changes in π electron density at the *para* C atom, thus:

$$\delta_{^1H} = k_{^1H}\Delta P_{CC} \tag{1}$$

$$\delta_{^{13}C} = k_{^{13}C}\Delta P_{CC} \tag{2}$$

where the two constants can be found empirically by comparing the shifts of ^{1}H and ^{13}C nuclei in cyclopentadienyl anion, benzene, tropyllium cation, and cyclo octatetraene dianion.[21,22] The value of $k_{^1H}$ depends upon the model chosen for the ring currents in these molecules, but almost certainly lies between 8·08 and 10·6 ppm/electron.[21–23] The value of $k_{^{13}C}$ has been estimated to be 160 ppm/electron. These values of $k_{^1H}$ and $k_{^{13}C}$ are unlikely to be seriously in error, hence the value of $\delta_{^1H}$ and $\delta_{^{13}C}$ provides an excellent means of determining the π-electron charge density at the *para* C atom. We have calculated $\delta_{^1H}$ using $\chi_{^1H} = 8{\cdot}08$ ppm/electron and $k_{^{13}C} =$ 160 ppm/electron. Table 3 shows the results for toluene using models i, iii and iv, also included for comparisons are the corresponding results for fluorobenzene, chlorobenzene, aniline and phenol. Again good agreement between experimental and calculated quantities requires that both the mesomeric and inductive effects of the methyl group be included as in model (iii.

Partial rate factors for nitration of xylenes

Introduction. The influence of Me substituents on reactivities has been treated by inductive models in the ω technique[7] and PPP frameworks[8] and by the ω techniques using a mesomeric and mesomeric–inductive model.[7] The inductive model of Flurry and Lyckos[8] whilst apparently giving a good account of the basicity of methyl benzenes cannot accommodate adequately experimental data of category (a), (b) or (c), and does not take into account the nuclear repulsion terms. As Dewar *et al.*

TABLE 3. CALCULATED AND OBSERVED ^{1}H AND ^{13}C CHEMICAL SHIFTS

Substituent	Model	Chemical shifts in p.p.m. relative to benzene			
		^{1}H		^{13}C	
		Calc.	Obs.	Calc.	Obs.
Me	iv	0·08		1·62	
	i	0·11		1·79	
	ii	0·20	0·18[24]	3·45	3·05[24]
F_{14}	i	0·09		1·74	
	iii	0·31	0·22[25]	6·10	4·40[25]
Cl[14]	i	0·10		1·98	
	iii	0·23	0·22[25]	4·64	2·00[25]
$\mathrm{NH_2}$[14]	i	0·08		1·60	
	iii	0·53	0·62[25]	10·56	9·50[25]
OH[14]	i	0·12		2·30	
	iii	0·46	0·48[26]	9·17	6·10[27]

have pointed out,[11] most of the early attempts to apply SCF–MO methods to calculating localization energies failed because of neglect of nuclear repulsion terms. In calculating localization energies the difference in pi bonding energy should be calculated and not the pi binding energy difference which does not allow for differing nuclear repulsions in the various Wheland intermediate cations for substitution in a given molecule.[11]

The argument in favour of a Wheland type intermediate as a model for the transition state in nitration of aromatic hydrocarbons have been set out by Dewar *et al.*[11] Previous theoretical investigations have concentrated on the correlation of localization energies with basicities of methylbenzenes.[7,8] However to some extent this is unsatisfactory since for polymethyl benzenes the sites of protonation within a given molecule are often not unambiguously assigned. The success of Dewars correlation of SCF calculated localization energies with partial rate factors for nitration of hydrocarbons makes it tempting to attempt a similar correlation for methyl substituted hydrocarbons. However as we have pointed out, it is somewhat surprising that such data is not available for the xylenes, and the lower limits on reactivity of para and meta xylene obtained by Olah seems unrealistic.

Experimental results. Isomer distributions have been studied in the temperature range 25–100° for the nitration ($\mathrm{HNO_3/HOAc}$) of the xylenes. Competitive nitrations at 25° between benzene and the xylenes have been carried out in order to determine partial rate factors. Table 4 shows the variation of isomer distributions with temperature for *o*- and *m*-xylene.

For *o*-xylene the 3 nitro isomer predominates at 25°, but as the temperature is increased the proportion of the 4 nitro isomer increases until at ~60° the two are produced in roughly equal amounts. At higher temperatures the 4 nitro isomer becomes the major product. A plot of ln [3-$\mathrm{NO_2}$/4-$\mathrm{NO_2}$ *o*-xylene] against $1/T$(°K) gives a reasonable straight line and from the slope an activation energy difference of 5·09 ± 0·34 kcals/mole may be calculated. The large errors involved make any detailed

TABLE 4. VARIATION OF ISOMER DISTRIBUTION WITH TEMPERATURE FOR THE NITRATION OF ORTHO XYLENE IN $HNO_3/HOAc$ MEDIA

T°C	*o*-Xylene Nitro-*o*-xylene $[3\text{-}NO_2]/[4\text{-}NO_2]$	*m*-Xylene Nitro-*m*-xylene $[4\text{-}NO_2]/[2\text{-}NO_2]$
25	2·67 ± 0·23	7·90 ± 0·30
40	1·75 ± 0·05	7·80 ± 0·31
50	1·32 ± 0·06	6·82 ± 0·02
60	1·07 ± 0·03	6·32 ± 0·20
70	0·86 ± 0·04	6·07 ± 0·07
80	0·71 ± 0·06	5·81 ± 0·05
100	0·61 ± 0·03	5·31 ± 0·15

interpretation of the entropy difference unjustified, but qualitatively it can be seen that for 3 substitution adjacent to a Me group relative to the unhindered 4 position there is a significant entropy difference.

Competitive nitrations at 25° give a ratio $k_{o\text{-xylene}}/k_{\text{benzene}}$ of 28·2 ± 3·8 and from the isomer distribution partial site factors for the 3 and 4 positions in *o*-xylene of 61·4 ± 8·8 and 23·3 ± 3·3 respectively, may be calculated.

In the case of *m*-xylene only two of the three possible nitro isomers were detected in the temperature range 25–100°. The major isomer is 4 nitro *m*-xylene, and the ratio of isomers varies to a relatively small extent. A plot ln $[4\text{-}NO_2/2\text{-}NO_2$ *m*-xylene$]$ against $1/T$(°K) gives an activation energy difference of 1·15 ± 0·16 kcals/mole, and the entropy difference must be quite small.

Competitive nitrations at 25° give a ratio $k_{m\text{-xylene}}/k_{\text{benzene}}$ of 399 ± 48 and from the isomer distributions, partial rate factors for the 2 and 4 positions in *m*-xylene of 268 ± 34 and 1063 ± 135 respectively, may be calculated.

For *p*-xylene the partial rate factor with respect to benzene at 25° obtained from competitive nitrations is calculated to be 54·9 ± 7·3.

Qualitative discussion of the experimental results. The partial rate factors for nitration of toluene and the xylenes are shown in Table 5.

TABLE 5. PARTIAL RATE FACTORS FOR NITRATION $HNO_3MeCOOH$ (25°) OF METHYLBENZENE

Compound	Position	Partial rate factor	Ref.
Benzene	—	(1)	—
Toluene	2	49·2	(12)
	3	2·4	
	4	69·4	
m-Xylene	2	268	This work
	4	1063	
o-Xylene	3	61·4	This work
	4	23·3	
p-Xylene	—	54·9	This work

It is of interest to compare the results with those previously obtained for protonation equilibria,[28] proto dedeuteration[28] and chlorination.[29]

We may define a reactivity constant σ_r and reaction constant $^*\rho$ by (3),

$$\log \frac{k_r}{k_{p\text{-xylene}}} = \sigma_r\, {}^*\rho \quad (3)$$

and defining the standard electrophilic substitution ($\rho^* = 1$) for the protonation equilibrium, reaction constants may be calculated for the other electrophilic reactions (Table 6). This indicates the much lower selectivity of the electrophile in nitration in HNO_3/HOAc media compared with the other reactions.

TABLE 6. REACTION CONSTANTS $^*\rho$ FOR ELECTROPHILIC SUBSTITUTION IN METHYLBENZENES

Reaction	$^*\rho$
Nitration HNO_3/HOAc, 25°	0·48
proto dedeuteration CF_3COOH—H_2SO_4–CCl_4,[28] 70°	0·83
Chlorination Cl_2/HOAc[29] (24°)	1·33

Quantitative discussion of the partial rate factor data. The theoretical calculations described in sections 2, 3 and 4 point to the fact that both inductive and mesomeric interactions (model (iii)) must be included to successfully accommodate experimental data in categories (a), (b) and (c). It is therefore of interest to investigate the application of this model to data of category (d).

TABLE 7. CATION LOCALIZATION ENERGIES OF Me SUBSTITUTED BENZENES

Compound	Position	$\Delta E_{\pi b}$ (eV)	$\Delta E_{\pi b} - \Delta E^{\circ}_{\pi b}$ (eV)
Benzene	—	22·512	0·0
Toluene	2	21·729	−0·783
	3	22·393	−0·119
	4	21·697	−0·815
o-Xylene	3	21·619	−0·893
	4	21·576	−0·936
m-Xylene	2	21·010	−1·502
	4	20·956	−1·556
	5	22·276	−0·236
p-Xylene	—	21·484	−1·028

In applying the inductive-mesomeric model (iii) to the localized intermediate cations, the inductive parameters were modified for the substituted carbon and the Me pseudo orbital in proportion to the pi electron density at the appropriate atom in the unsubstituted benzenium cation, this being the natural extension to charged species of the method which has previously been described for neutral species.

Table 7 shows the cation localization energies $\Delta E_{\pi b}$ (calculated as the difference in pi bonding energy between the neutral molecule and substituted benzenium cation), and also the differences with respect to benzene taken as standard.

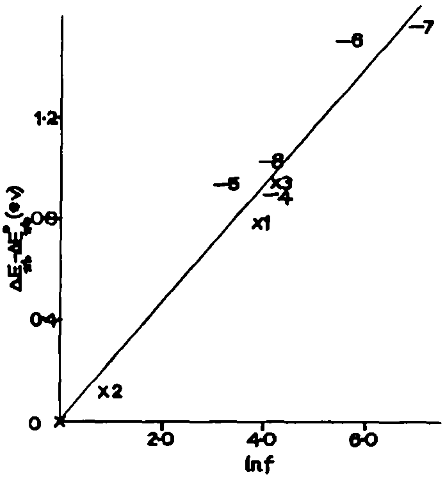

FIG. 1 Plot ln f (partial rate factors for nitration HNO_3/CH_3COOH at 25°C) versus $\Delta E_{\pi b} - \Delta E^{\circ}_{\pi b}$ (in eV).

Key: (1) Toluene 2 position
(2) Toluene 3 position
(3) Toluene 4 position
(4) *o*-Xylene 3 position
(5) *o*-Xylene 4 position
(6) *m*-Xylene 2 position
(7) *m*-Xylene 4 position
(8) *p*-Xylene

In Fig. 1 ln f (partial rate factors for nitration HNO_3/HOAc, 25°) are plotted versus relative cation localization energy. The partial rate factors cover a range of $\sim 10^3$ and the correlation is surprisingly good considering the many approximations inherent in the localization energy approach, and it should be noted that the straight line passes close to the origin. The points falling furthest from the linear correlation are (5) and (6), the 4 position in ortho xylene and 2 position in *m*-xylene respectively. For both sites the reactivity is lower than predicted on the basis of localization energy and for the 2 position in *m*-xylene this almost certainly arises from steric compression at this site, the main contribution coming from the enthalpy term, since the temperature variation study shows that the entropy difference for substitution at the 2 and 4 positions is quite small. It is interesting to note that the 4 position in *o*-xylene also appears to behave somewhat anomalously in proto detritiation.[30] The fact that the 3 position in *o*-xylene falls close to the straight line (and as we have pointed out there is a significant entropy difference between the 3 and 4 positions in *o*-xylene), emphasizes the fact that the localization approach does not require entropy differences to be the same for substitution at different sites within a molecule, but that the ratio of partition functions for the two reactions should be equal.

In conclusion it can be seen that a unified picture of the electronic effect of a methyl substituent can be obtained within the PPP formalism by inclusion of both mesomeric and inductive contributions, as developed in model (iii).

6. EXPERIMENTAL

Materials

Nitric acid. HNO_3 (10 ml, *d* 1·51) was mixed with H_2SO_4 (10 ml, *d* 1·84) and distilled (room temp, 0·001 mm) into a liquid air cooled receiver containing H_2SO_4 (5 ml, *d* 1·84). HNO_3 was distilled from this receiver (room temp, 0·001 mm) into a liquid air cooled flask containing glacial HOAc (1 ml), until 0·63 g had been transferred. The colourless soln of HNO_3 in HOAc thus obtained was allowed to melt and immediately added to the soln to be nitrated.

Acetic acid and benzene. British Drug Houses ANALAR HOAc and benzene were used without further purification.

o-Xylene, *m*-xylene and *p*-xylene were dried before use with P_2O_5 and distilled. They were shown to be pure by analytical gas chromatography.

Analytical nitrations. The nitrations were conducted in a thermostat controlled by a Jumo contact thermometer, with temp control ±0·01°. The reaction mixtures were stirred c. 1200 rpm and the amounts of substrate (*o*-, *m*-, *p*-xylene, alone or with benzene) were each 0·01 mole. The substrates were dissolved in HOAc (25 ml) and allowed to equilibrate at the required temp before treating drop-wise with a soln of HNO_3 (0·63 g, 0·01 mole) in HOAc (1 ml), prepared as above. The reaction mixture was left until coloration (yellow, orange or red, depending on substrates) showed that some nitration had occurred. (We allowed less than 5% reaction to occur in competitive runs so that our calculations of partial rate factors would be valid.)

Preparation of sample for analysis

The reaction mixtures were quenched by pouring into ice-water (200 ml) with stirring. The suspensions were neutralized with Na_2CO_3 before extraction with ether (4 × 100 ml). The ether extracts were washed with water (2 × 100 ml) and these washings were extracted with ether (50 ml). The total ether solns were dried ($MgSO_4$), filtered, and the $MgSO_4$ residue washed with ether (30 ml). The combined ether extracts were distilled, and the cooled residual oil dissolved in a small amount of $CHCl_3$. This procedure was checked with standard solns of reaction products. Within the estimated error of the gas chromatographic analyses, the compositions of the solns before and after extraction were the same.

Preparative reactions

Preparative nitrations were carried out on each hydrocarbon using the same experimental procedure as above. A larger amount of material was used with the temp maintained at 100° for 4 hr.

Gas chromatography

All analyses were made using a single column Pye 104 gas chromatograph, fitted with a flame ionization detector. This was coupled to a Honeywell–Brown recorder (−1 to +10 mV) fitted with a Kent Chromalog integrator. The columns employed for analyses were (a) 5% neo-pentylglycol adipate on Celite (90–100 mesh), 5 ft by $\frac{1}{16}$ in i.d. and (b) 10% methyl silicone rubber gum on Celite (90–100 mesh), 10 ft by $\frac{1}{16}$ in i.d. N_2 was used as carrier gas at a flow-rate of 60 ml/min.

We have calibrated the detector for all the products of the reactions studied. For all the nitro-isomers tested, the weight responses were identical, for each particular hydrocarbon, to within 1%, and linear over the range 0·1–10 μl sample injected. Peak areas, measured with the integrator or from the recorder traces with a planimeter, were multiplied by the appropriate correction factor for mol wt differences and the difference in response for nitro-isomers of different hydrocarbons. Isomer distributions were recorded as product ratios and the standard deviations estimated from a minimum of three analyses.

Identification of products from analytical reactions

The products from preparative scale nitrations of the xylenes were separated by preparative scale GLC. The products were identified by comparison of IR spectra and retention times, with those of authentic samples.

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REFERENCES

[1] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953).

[2] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).

[3] D. P. Craig and G. Dogget, *Mol. Phys.* **8**, 485 (1964).

[4] [a] J. N. Murrell and M. Godfrey, *Proc. Roy. Soc.* **A278**, 71 (1964);
[b] J. N. Murrell and D. R. Williams, *Ibid.* **A291**, 224 (1966).

[5] R. L. Flurry, *Theoretica Chim. Acta* **9**. 96 (1967).

[6] P. Lindner and O. Martensson, *Ibid.* **7**, 352 (1967).

[7] S. Ehrenson, *J. Am. Chem. Soc.* **83**, 4493 (1961), *Ibid.* **84**, 2681 (1962).

[8] R. L. Flurry and P. G. Lykos, *Ibid.* **85**, 1033 (1963).

[9] J. Petruska, *J. Chem. Phys.* **34**, 1120 (1961).

[10] D. W. Turner, *Determination of Organic Structures by Physical Methods* (Edited by F. C. Nachod and W. D. Phillips) Vol. 2. Academic Press, N.Y. (1962).

[11] M. J. S. Dewar and C. C. Thompson, *J. Am. Chem. Soc.* **87**, 4414 (1965).

[12] G. A. Olah, S. J. Kuhn, S. H. Flood and J. C. Evans, *Ibid.* **84**, 3687 (1962).

[13] P. G. E. Alcorn and P. R. Wells, *Austral. J. Chem.* **18**, 1377 (1965).

[14] D. T. Clark and J. W. Emsley, *Mol. Phys.* **12**, 365 (1967).

[15] J. N. Murrell, *The Theory of Electronic Spectra of Organic Molecules*, Methuen (1963).

[16] F. H. Field and J. L. Franklin, *Electron Impact Phenomena.* Academic Press, N.Y. (1957).

[17] M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.* **20**, 837 (1952).

[18] H. H. Jaffe and J. Hinze, *J. Am. Chem. Soc.* **84**, 540 (1962).

[19] R. Pariser, *J. Chem. Phys.* **24**, 250 (1956).

[20] A. L. H. Chung and M. J. S. Dewar, *Ibid.* **42**, 756 (1965).

[21] G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *Ibid.* **82**, 5846 (1960).

[22] H. Spiesecke and W. G. Schneider, *Tetrahedron Letters* No. 14, 468 (1961).

[23] B. P. Dailey and T. K. Wu, *J. Chem. Phys.* **41**, 2796 (1964).

[24] T. D. Alger, D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.* **88**, 5397 (1966).

[25] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* **35**, 722 (1961).

[26] J. C. Schug and J. C. Deck, *Ibid.* **37**, 2618 (1962).

[27] P. C. Lauterbur, *J. Am. Chem. Soc.* **83**, 1846 (1961).

[28] E. L. Mackor, P. J. Smith and J. H. van der Waal, *Trans. Faraday Soc.* **53**, 1309 (1957).

[29] P. B. de la Mare and P. W. Robertson, *J. Chem. Soc.* 279 (1943).

[30] H. V. Ansell and R. Taylor, *Ibid.* (B), 526 (1968).