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THE GEOMETRY AND ELECTRONIC STRUCTURE OF SUBSTITUTED SCHIFF'S BASES†

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Abstract—One electron Extended Hückel Molecular Orbital (EHMO) theory has been used to study the conformational geometry of five benzal-*p*-*X*-aniline (X = H, Me_3, Cl, Br, Me_3O) Schiff's bases. The electronic structure predicted by this method was used as a guide for a least squares resolution of the observed electronic (UV) spectra. The resultant resolved spectra are discussed in terms of correlations of band shifts with substituent properties.

INTRODUCTION

THE EHMO theory has found wide application in both organic and inorganic chemistry during the last few years[1] and has recently been the subject of critical reviews both on the theory[2] and on applicability.[1] In view of these reviews and on the experience of the wide range of systems studied with this method, it was felt that it could be used to investigate the problem of the geometry and electronic structure of substituted benzal-anilines.

The crucial approximation of Hückel theory is the rewriting of the Hamiltonian as a sum of one electron terms

$$H_{op} = \sum_{\mu}^{2n} - \tfrac{1}{2}\nabla_{\mu}^{2} + V(\mu, \lambda) \simeq \sum_{\mu}^{2n} - \tfrac{1}{2}\nabla_{u}^{2} + \sum_{\mu}^{2n} V_{eff}(\mu) \equiv \sum_{\mu}^{2n} H_{eff}(\mu) \qquad (1)$$

This approximation assumes the potential of an electron (μ) is a function of its coordinates alone with an averaged interaction with the other electrons (λ). The effective Hamiltonian, $H_{eff}(\mu)$, is not defined explicitly, but is determined by its matrix elements. In the atoms-in-molecules approach,[3] the diagonal element H_{pp} is interpreted as the valence state ionization energy of the pth AO while the off-diagonal elements are approximated some way. Of the several formulae suggested[4,5] the Wolfsberg–Helmholtz form[3]

$$H_{pq} = kS_{pq}(H_{pp} + H_{qq})/2 \qquad (2)$$

where k is a variable parameter and S_{pq} the overlap between the pth and qth AO is the most popular at this time[6–9] and has been selected for this work.

The complete set of valence shell AO, whether occupied or not in the atom, was included for each nucleus. The AO were assumed to be Slater-type-functions

$$\eta_{nlm}(r, \theta, \psi) = A_n r^{n-1}\, e^{-\alpha r}\, Y_{lm}(\theta, \psi) \qquad (3)$$

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All inner AO were neglected other than for their shielding effect on the nucleus. This approximation is relatively accurate, as is borne out by *ab initio* calculations utilizing large basis sets. The lowest lying MO correspond very closely to the core AO of the various heavy atoms, both in shape and energy.[10,11]

CALCULATIONS

Input parameters. The input parameters for the atoms have been tabulated in Table 1. Slater's rules[12] were used to calculate exponents for first and second row atoms but due to the large difference between these values and LCAO(STO)-MO-SCF optimized values[13] for higher row elements, optimized values were used for s and p exponents of chlorine and bromine. Spectroscopic data† provided coulomb integrals for C, N, O and H, for the s and p orbitals of Cl_2 and for the p orbital of Br_2. Since a linear relationship was found between spectroscopic values and calculated values,[15] an equivalent value for the s AO of this latter atom was obtained. In order to include d orbitals on Cl_2 and Br_2 the d exponent and coulomb integral were simultaneously varied in Cl_2 and Br_2 to obtain optimum values. Since performing this, a value for the coulomb integral for Cl 3d has been published.[16] This value (−2·114) compares well with the value (−2·0) obtained in the present optimization.

Table 1. Orbital exponents and Coulomb integral values for EHMO calculations

Atom	AO Type	Exponent	Coulomb integral
H	1s	1·000	−13·60
C	2s	1·625	−21·01
	2p	1·625	−11·27
N	2s	1·950	−26·00
	2p	1·950	−12·40
O	2s	2·275	−32·30
	2p	2·275	−14·80
Cl	3s	2·359	−24·02
	3p	2·039	−15·08
	3d	1·100	−2·00
Br	4s	2·638	−26·40
	4p	2·257	−13·70
	4d	1·200	−2·50

Finally, the parameter in the Wolfsberg–Helmholz formula [2] was chosen as 1·75. This is the value found by Hoffmann[7] to be optimum for organic molecules.

*Geometry of benzal-*p-X-*anilines.* Since no crystallographic data on the geometry of benzal–analine is available, the conformation adopted for this study was arrived at by a combination of estimating some parameters and optimizing others. This "core" structure was then used for the other compounds replacing the para-hydrogen of the aniline ring with the appropriate substituent group (—X).

The benzene rings were assumed to be planar regular hexagons. All bond lengths were estimated from x-ray data on compounds containing analogous structures; these are listed in Tables 2 and 3. All bond angles except ϕ—N=C, ϕ—C=N and ϕ—C—H were estimated in a similar manner and are also listed in Tables 2 and 3.

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† Our values are a hybrid set taken from several references including some averaged values.[14]

TABLE 2. GEOMETRICAL PARAMETERS FOR BENZAL-ANILINE

Parameter*	Value	Ref.†
a	1·45 Å	stilbene, chlorobenzaldoxime benzonitrile (1·42), toluene (1·52), dibenzyl (1·52)
b	128°	optimized
c	116°	optimized
d	1·07 Å	paraffinic C—H (trisubst. C)
e	1·31 Å	chlorobenzaldoxime 6-carbamoyl-3-pyridazone (1·32) creatine (1·30)
f	156°	optimized
g	1·42 Å	4-isopropyleneaminophenol, azobenzene (1·41) phenylisocyanate dimer (1·41)
h	1·38 Å	*p*-aminophenol, *p*-dinitro-benzene *p*-nitro-aniline, *p*-dichloro-benzene
i	1·08 Å	benzene plus cpds for h above
j	120°	assumed (cf. benzene)
k	1·39 Å	toluene, stilbene, dibenzyl, diphenylacetylene, azobenzene

* cf. Fig. 1 for definition of letters.

† All values taken from Tables (35); see this Ref. for original refces.

TABLE 3. GEOMETRICAL PARAMETERS FOR *p*-*X* SUBSTITUENT ON BENZAL-*pX*-ANILINES

$-p$X	parameter	Value	reference*
—Me$_3$	ϕ—C	1·50 Å	toluene (1·52), *p*-nitrotoluene, 4,4′-dimethylbenzyl (1·52), *p*-xylene, *p*-toluidine HCl (1·49)
	C—H	1·10 Å	paraffinic C—H (monosubstituted carbon)
—OMe$_3$†	ϕ—O	1·38 Å	dimethoxybenzene, di-*p*-anisylnitricoxide (1·40), D,L-isocryptopleurinemethiodide
	O—C	1·43 Å	paraffinic O—C, di-*p*-anisyl-nitricoxide (1·44)
	C—H	1·10 Å	as for Me above
	CH$_3$		
	ϕ—O	121°	1,4-dimethoxybenzene
—Cl	ϕ—Cl	1·70 Å	1,5-dichloroanthracene, chlorobenzene
—Br	ϕ—Br	1·86 Å	bromobenzene, *p*-dibromobenzene

* See footnote (†) to Table 1.

† Two conformations of the Me-hydrogens were considered.

The ϕ—N=C angle and the co-planarity of the two benzene rings has been the subject of much discussion.[17–25] Any steric hinderance associated with this angle being 120° may be removed either by rotation of the phenyl ring out of the plane of the rest of the molecule or by opening of this bond angle. Simple Hückel MO (SHMO) calculations[17] have been performed on this compound, which were used to make an approximate interpretation of the UV spectrum; this assumes implicitly the geometry of II in Fig. 2. Experimental evidence, namely the instability of the cis isomer and anomalies of dipole moment of substituted compounds, has been cited to show that the ϕ—N═C valence angle is indeed 180°[18, 19] (cf III in Fig. 2), as assumed in the SHMO. Other papers on the structure of araldehyde anils have also considered a structure with the two rings coplanar.[20, 21]

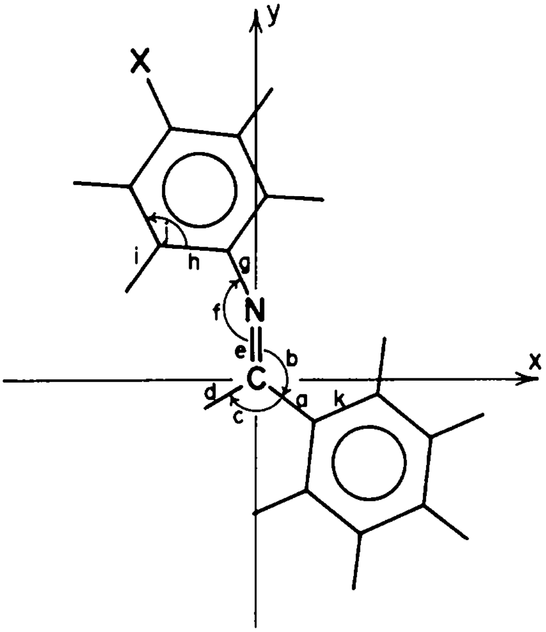

FIG. 1 Geometry of benzal-aniline.

Smirnov and Ismailski[24] were the first to postulate that the anomalies may be due to acoplanarity of the two rings. Several papers have given support to their claim both on the basis of experimental evidence, including interpretation of spectra,[23] half wave potentials,[24] and SHMO calculations[25] where the lone pair was included in the system. This structure is that shown as IV in Fig. 2. On the basis of these SHMO results, the spectrum is better interpreted using this geometry.

In the present work a series of calculations have been carried out, in which the two angles ϕ—N═C and ϕ—C═N were both kept 120° and the Ph group of the aniline moiety rotated up to 35° out of the plane of the rest of the molecule. A conformation corresponding to a 5° rotation lowered the energy by 0·3 kcal/mole which seemed negligible to justify an acoplanar geometry. Also, since the isoelectric species *trans*-stilbene[26] and *trans*-azobenzene[27] have planar structures, it seems reasonable that the difficulties encountered by the previous authors[23, 25] were due rather to the method (i.e. SHMO) than to the acoplanarity of the rings, as claimed. Accordingly, in the further work a planar geometry was assumed throughout, and the anomalies ascribed to ϕ—N═C bond angle opening.

In order to test this hypothesis, a conformation study was performed. Initially, the ϕ—N═C and ϕ—C═N angles were varied simultaneously, the ϕ—N═C from 120°

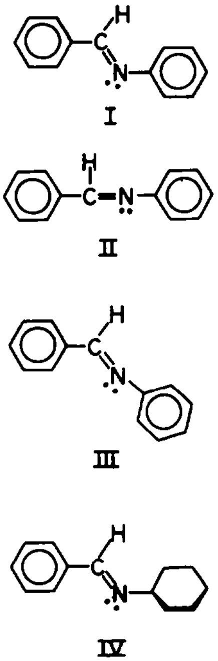

FIG. 2 Postulated geometries of benzal-aniline.

to 180°, the ϕ—C=N from 120° to 130°. A total of 23 points were calculated, mostly following the line of steepest descent from (120°, 120°) to the minimum, but also surrounding the minimum and also a few scattered points to clarify the nature of the surface. An approximate contour diagram was drawn to indicate the shape of this surface. This diagram is shown in Fig. 3 where the contour lines represent the energies, as marked in Kcal/mole, above the minimum conformation. It can be seen that the optimum ϕ—C=N angle is 128°, the same as in *trans*-stilbene, while the ϕ—N=C angle is spread out to 156°. The ϕ—C—H angle was then varied for these values of ϕ—C=N and ϕ—N=C, and the optimum angle found to be 116° (while calculating the surface this was made to bisect the ϕ—C=N angle).

Although the surface is not complete so far as predicting the existence of a stable *cis* form, a prediction of a low energy barrier for the conversion of *trans* to *cis* of approximately 4 kcal/mole is indicated. This value is based on the energy of the conformer with ϕ—N=C angle 180°, ϕ—C=N angle 120°. This predicted barrier is somewhat lower than the expected experimental value since the activation energy for the *cis–trans* isomerization amounts to 13·5–17·5 kcal/mole.[28,29] Nevertheless the qualitative agreement readily overcomes one objection to the coplanar structure.

trans-*Stilbene* and trans-*azobenzene*. In order to demonstrate the validity of the prediction of a large ϕ—N=C angle, the symmetric variation of the two ϕ—X=X angles in *trans*-stilbene and *trans*-azobenzene was investigated. Other geometrical parameters were kept the same as for benzal-aniline with reported bond lengths for C=C and N=N (1·33 Å and 1·23 Å respectively). The minimum energy conformers were found to have angles of 131° for *trans*-stilbene, 3° larger than experimental and

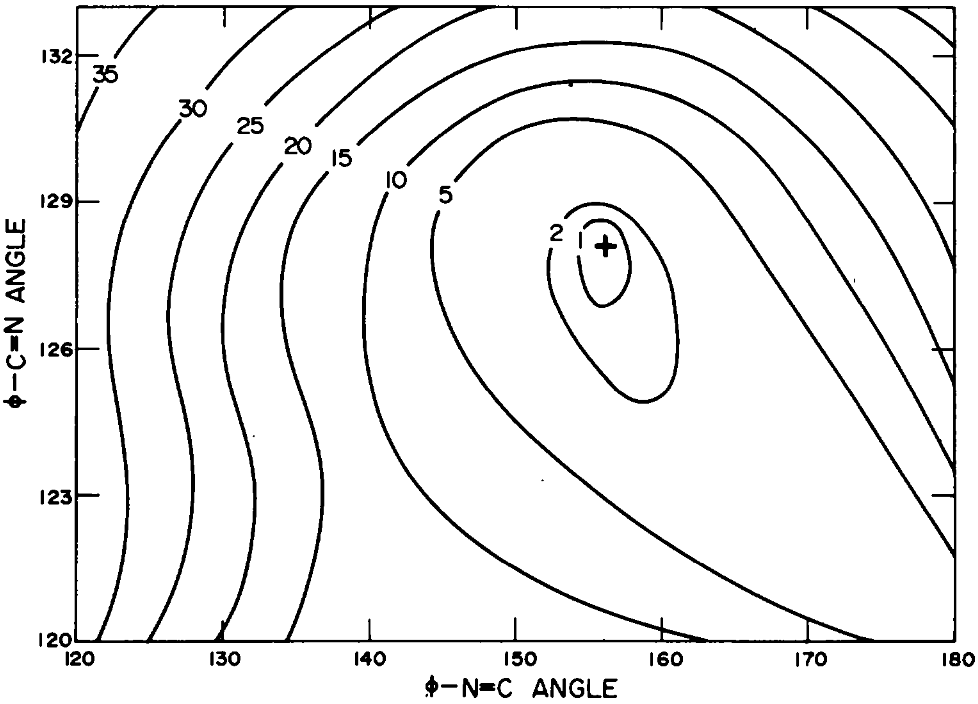

FIG. 3 Energy surface of benzal-aniline.

135° for *trans*-azobenzene, 15° larger than experimental. These results lend confidence to the prediction that the ϕ—N═C angle in benzal-aniline is anomalously large, although not necessarily so large as the 156° predicted.

*The electronic structure of benzal-*p-X-*anilines.* Orbital energy level diagrams for the five compounds (X = H, Me, Me_3O, Cl, Br) are given in Fig. 4. In this diagram the dotted line separates filled and empty levels and closely spaced levels are indicated by a broken line. The n_N and all the π-levels have been labelled.

The MO of interest to the electronic spectra have been plotted as electron density contours. The density of the MO was calculated from

$$\phi_i^2 (x, y, z) = \text{occy}\,(i)\,[\sum_r^{AO} c_{ir}\, \eta_r\, (x, y, z)]^2 \tag{4}$$

Fig. 5 shows the five highest occupied σMO of benzal-aniline as a cross section through the plane of the molecule. Similar plots for the four highest occupied πMO and four lowest π^*MO as a cross section 1 Å above the molecular plane are included as Figs 6 and 7. In these plots the outside contour value is 10^{-6} electrons per cubic bohr with inner contours increasing by a factor of 10. The two middle rows of Figs. 6 and 7 depict MO which are analogous to the two sets of degenerate MO of *trans* stilbene.

On the basis of these diagrams a correspondence of MO levels may be made as shown in Fig. 4. From this correspondence identical transitions may be determined and electronic spectra predicted (Fig. 8). In all cases the spacing of the $\pi^* \leftarrow \pi$ transition (long lines) are relatively the same while minor differences occur in the $\pi^* \leftarrow \sigma$ transitions (short lines).

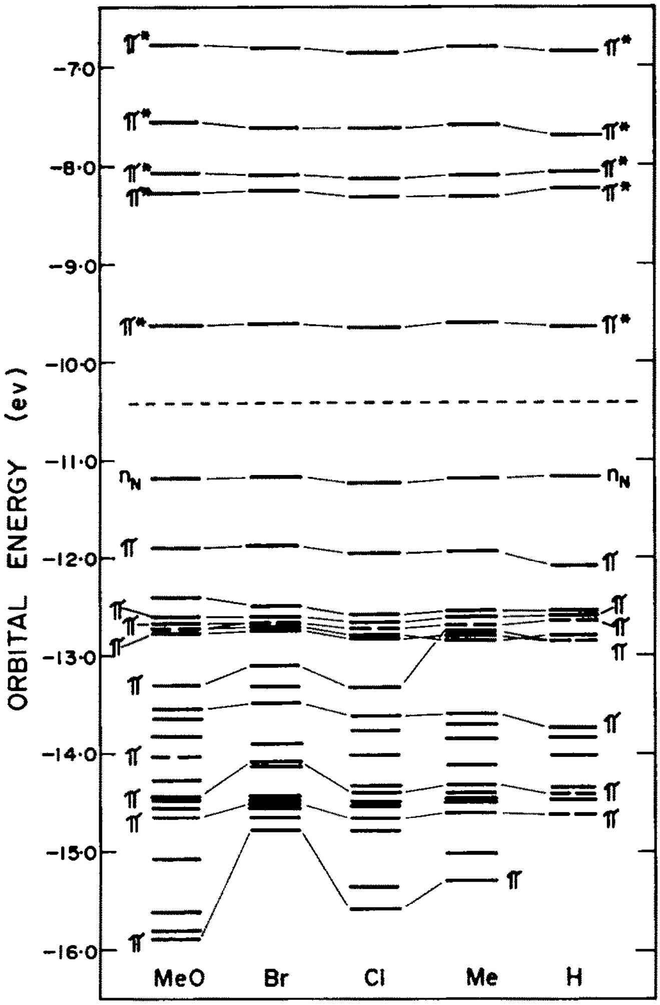

FIG. 4. Orbital energies for benzal-*p*-X-aniline compounds.

UV spectra

The spectra of the five compounds in heptane are given in Fig. 9. These spectra have the same general shape but show large differences in intensity and fine structure. The spectra were also recorded in methanol but no appreciable change was noticed.

Resolution of spectra. Although there is no consideration that will predict the shape of electronic spectral bands, the most common curve used to approximate them is a gaussian curve. A numerical least squares technique[30] was adopted that would optimize an initial set of parameters to best fit the curve. Several initial sets were chosen based on the EHMO predictions. This showed that while there was no set that was completely unique, the parameters of the large bands were relatively invariant.

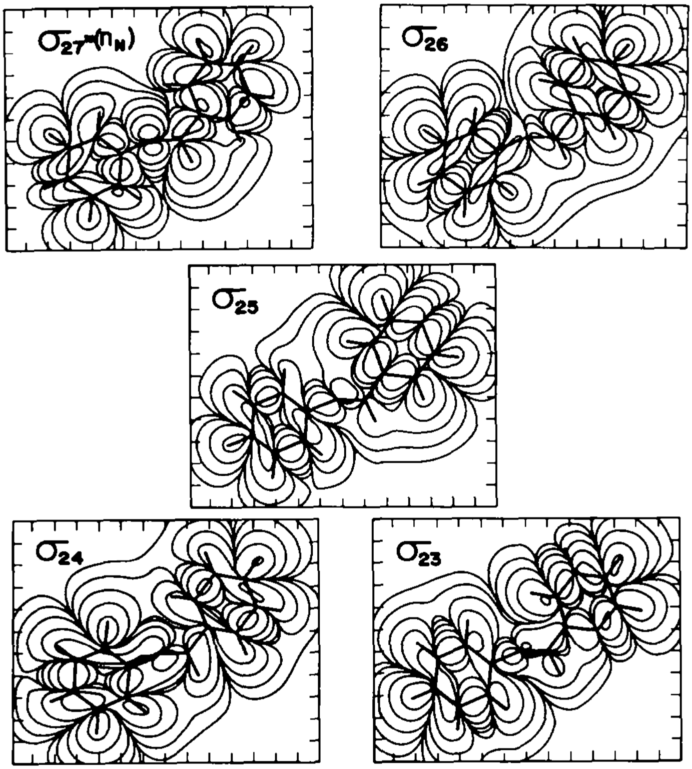

FIG. 5 Highest occupied σ MO for benzal-aniline (contours are drawn in the plane of the molecule).

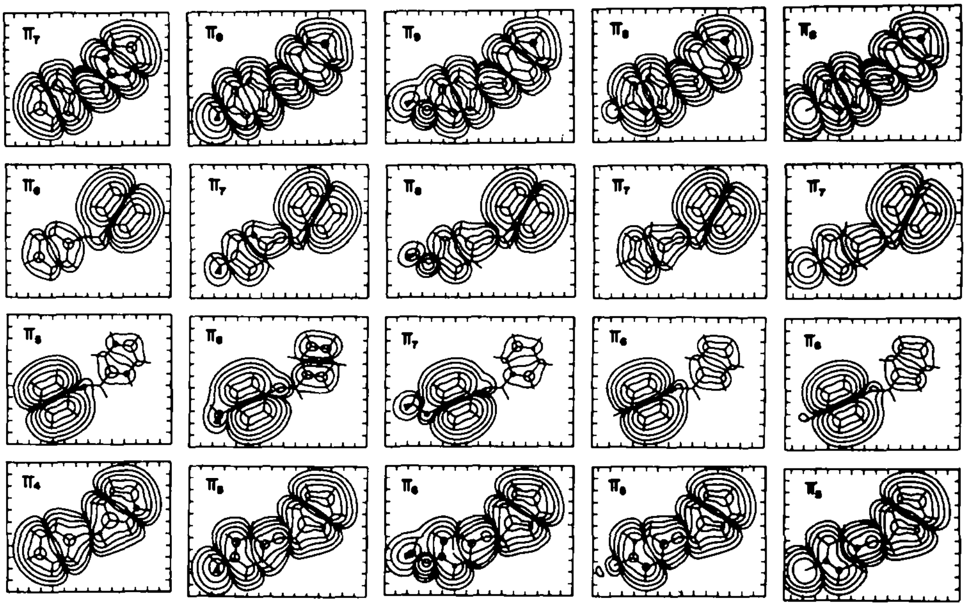

FIG. 6 Highest occupied π MO for benzal-*p*-X-anilines (from left to right $X = H, CH_3, CH_3O$, Cl, Br; contours are drawn 1 Å above the plane of the molecule).

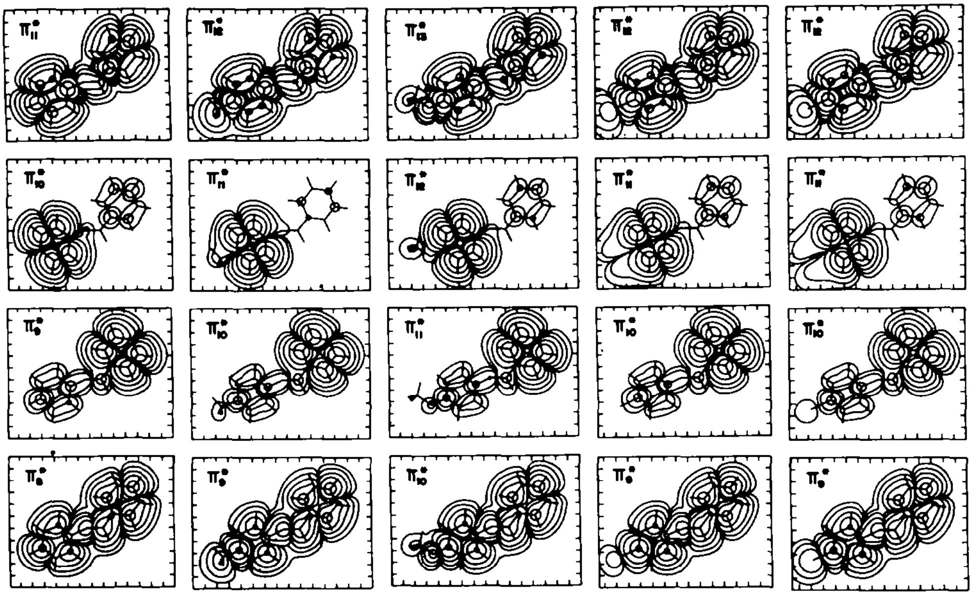

FIG. 7 Lowest virtual (π^*) MO for benzal-p-X-Anilines (from left to right X = H, CH_3, CH_3O, Cl, Br; contours are drawn 1 Å above the plane of the molecule).

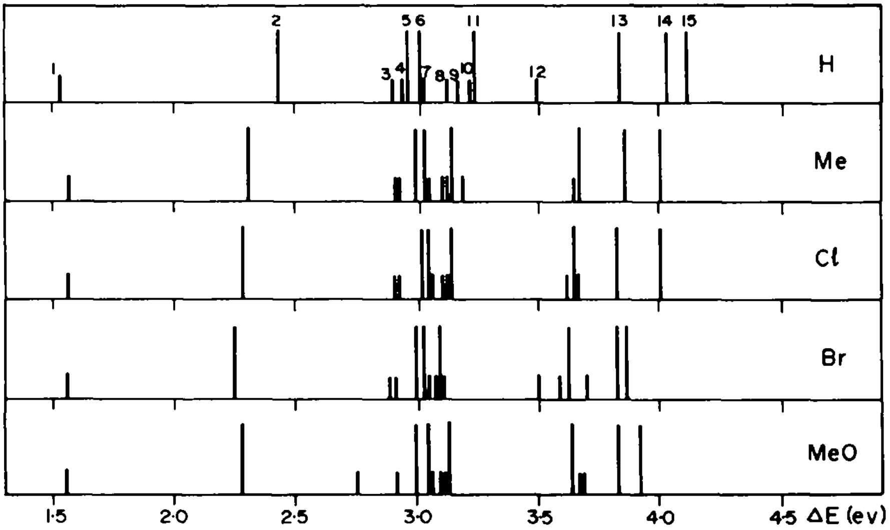

FIG. 8 Calculated (EHMO) transition energies.

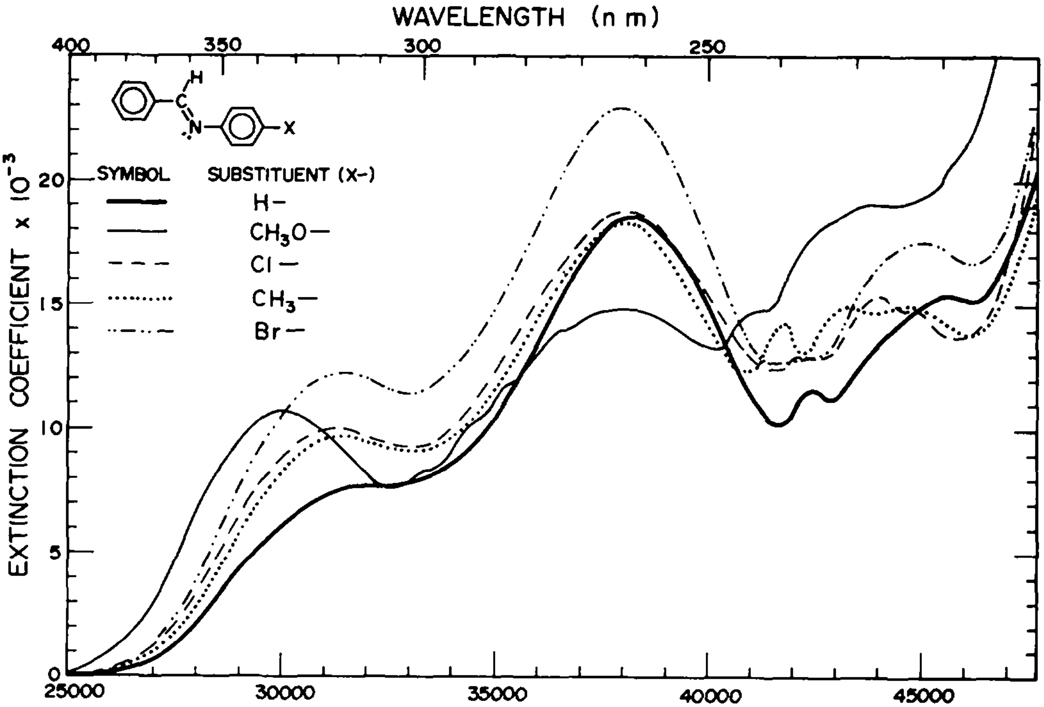

Fig. 9 Spectra in heptane.

We have included the smaller bands as predicted by the set giving the smallest standard error as defined by (5) for completeness only.

$$\text{standard error} = \left[\frac{\sum_{i}^{\text{data pts}} (I_{obs}(i) - I_{calc}(i))^2}{\text{No. data pts}}\right]^{\frac{1}{2}} \tag{5}$$

The resolved spectrum of benzal-aniline in heptane is given in Fig. 10; those for the other compounds are not included. All five spectra have been drawn schematically in Fig. 11. A comparison of Figs 8 and 11 permits a one-to-one assignment for the transitions.

Correlations of transition energy with substituent properties. In order to investigate further the electronic spectra of these compounds, the $\pi^* \leftarrow \pi$ band shifts ($\Delta\Delta E$) of the substituted compounds relative to benzal-aniline were plotted against substituent properties. The properties included are group ionization potential (taken for the corresponding value for substituted methane,[31] Hammett's σ_p,[32] Hammett's ($\sigma_p - \sigma_m$) and Bloor's empirical spectroscopic σ_s^+.[33] Hammett's ($\sigma_p - \sigma_m$) is considered to represent the resonance effect of the substituent alone. The values of the properties are tabulated in Table 4 while the plots are given in Fig. 12. It should be noted that for three of the plots, ionization potential, ($\sigma_p - \sigma_m$) and σ_s^+, the points are in the same order (MeO, Br, Cl, Me, H) but differently spaced, while for σ_p they are in the order: MeO, Me, H, Cl, Br. It can be seen that the transition energy dif-

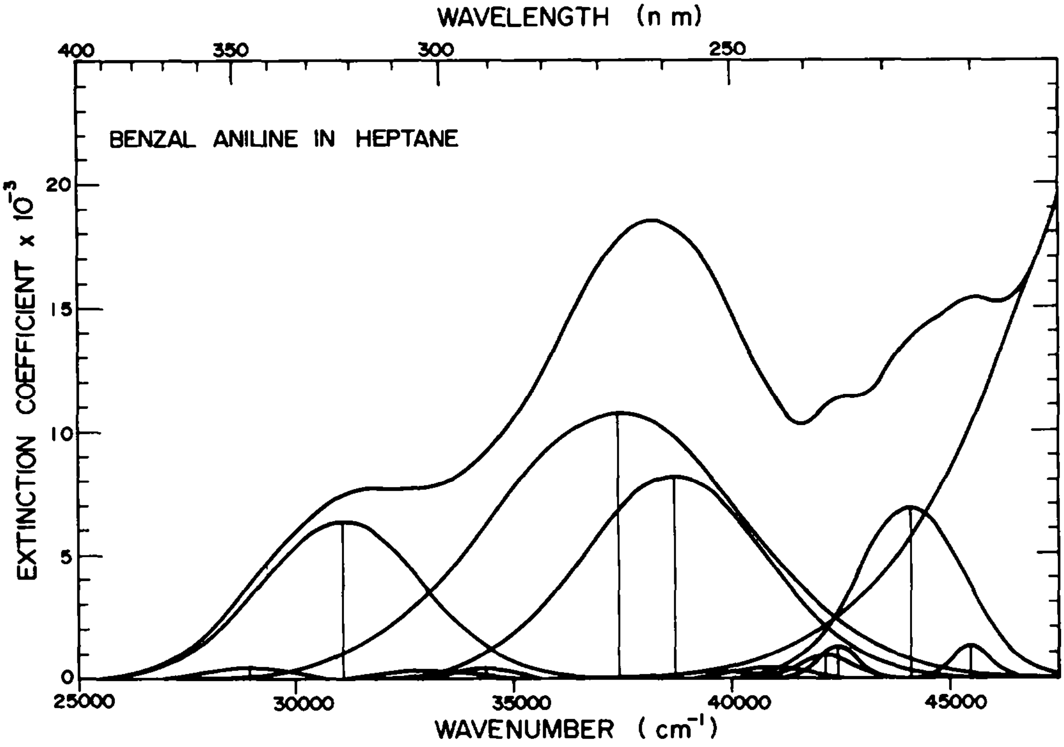

FIG. 10 Benzal-aniline in heptane.

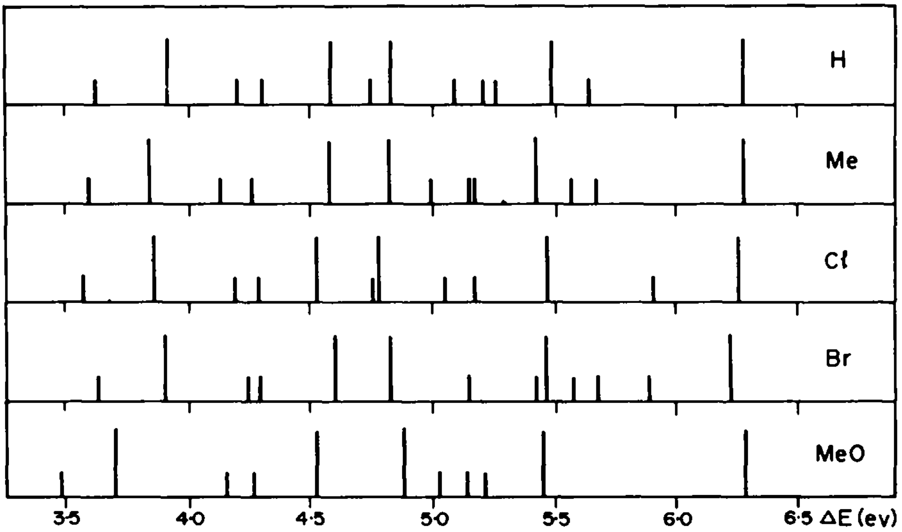

FIG. 11 Observed transition energies in heptane.

TABLE 4. ELECTRONIC PROPERTIES OF SUBSTITUENTS

Substituent Property	MeO	Br	Cl	Me	H
IP (eV)	10·5	11·2	11·3	11·5	13·1
$\sigma^+_{hept.}$	0·55	0·26	0·22	0·19	0·0
$\sigma^+_{meth.}$	0·58	0·22	0·16	0·18	0·0
$\sigma_p - \sigma_m$	−0·383	−0·159	−0·146	−0·101	0·0
σ_p	−0·268	0·232	0·227	−0·170	0·0

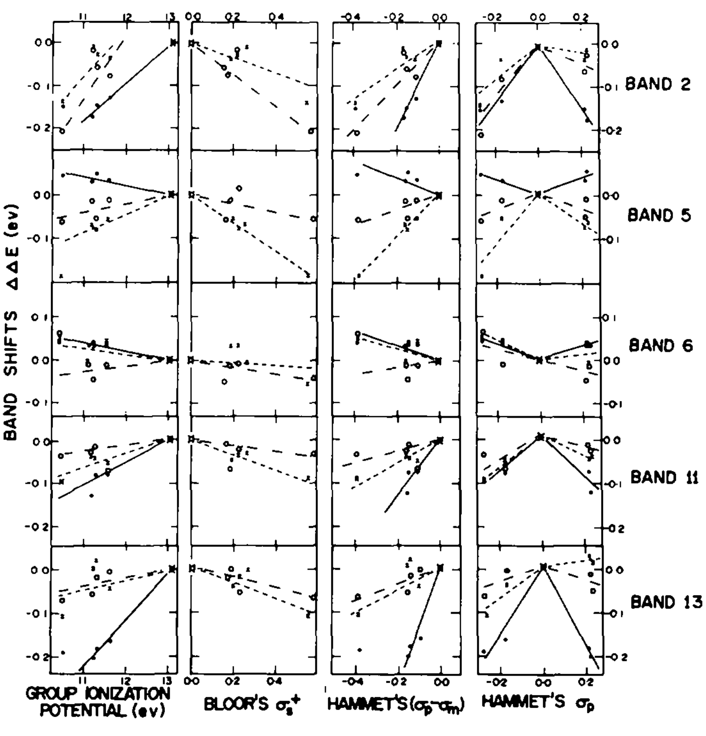

FIG. 12 Correlation of ΔΔ*E* with substituent properties (—● calculated; — — × in heptane; – · · ○ in methanol).

ferences predicted by the EHMO method correlate best with group ionization potentials. This is to be expected since atomic ionization energies were used as input; hence any difference between the calculations is directly related to ionization energies. The differences of transition energies obtained by the spectral resolution correlate best with the empirical spectroscopic sigma values, σ_s^+. This is also to be expected since these values are average values for several compounds[33] for the correlation of ΔΔ*E* with substituents. These correlations are a good indication of the reliability of this method. Since ΔΔ*E* represents the second difference of numbers of large magnitude, the minor deviations of the points from the lines drawn through them are easily acceptable.

It is important to note that no correlations were found with Hammett's σ_p. In all cases the line is broken at benzal-aniline ($\sigma_p = 0$). This is in direct contradiction to reported correlations of experimental band position of the first $\pi^* \leftarrow \pi$ transition to Hammett's σ_p.[25] These authors, however, take band position from λ_{max}, and not from a resolution of the curve. Since this band appears as a broad shoulder, not an actual maximum, and since this difference plot is very sensitive to minor differences in band position, a correlation obtained in this manner is subject to doubt.

The desire to force the calculated transition energies to correlate with σ_p was one reason encouraging these authors to rotate the aniline ring out of planarity with the benzaldehyde ring. Since the experimental values, obtained by a numerical resolution technique, do not correlate with σ_p, this would suggest that their hypothesis was incorrect. The first $\pi^* \leftarrow \pi$ band is more isolated thus there is a good reason to have high confidence in the parameters for this band.

A second reason for rotating aniline ring was in order to explain the "absence" of the first $\pi^* \leftarrow n_N$ band at the low energy tail of the spectrum. Since their non-planar structure conjugates with all the nitrogen AO this band disappears. This band, however, has been found in this investigation under the tail of the first $\pi^* \leftarrow \pi$ band.

The failure of half wave potentials of benzal-*p*-X-aniline compounds to correlate with σ_p[22] has also been noted. This has also been cited as evidence for the aco-planarity of these rings. It is thus indicated that this conclusion is incorrect, and is due to failure to understand the electronic structure of these compounds. This attempted correlation gave a broken line similar to the correlations in this work.

It was found that for the isoelectric compounds parasubstituted azobenzenes which are known to be planar[27] and for which the first two $\pi^* \leftarrow \pi$ bands are clearly defined structures, no correlation between band position and Hammett's σ_p could be made (the attempt at correlation was made from values reported for these compounds[34]). In the light of this information, it is not to be expected that such a correlation should be found for benzal-*p*-X-aniline compounds.

It should be recalled that both Hammett's σ_p and σ_m were correlated with reference to differences between two electronic ground state species (in equilibria the initial and final state, in kinetics the initial and transition state). In spectroscopic work,

TABLE 5. CHARACTERISTICS OF ϕ—CH=N—ϕ—X COMPOUNDS

		Elementary composition				
		Calculated/Obtained			m.p.°	
—X	Formula	C	H	N	Reported[36]	Obtained
—H	$C_{13}H_{11}N$	86·15	6·12	7·73	53·5	51·0–53·3
		86·26	6·08	7·91		
—Me	$C_{14}H_{13}N$	86·12	6·71	7·17	35·0	31·7–32·8
		86·44	6·63	6·92		
—OMe	$C_{14}H_{13}NO$	79·60	6·20	6·63	72·0	70·7–72·0
		78·97	6·12	7·03		
—Cl	$C_{13}H_{10}NCl$	72·40	4·67	6·49	62·0	59·8–60·7
		72·42	4·66	6·30		
—Br	$C_{13}H_{10}NBr$	60·02	3·88	5·38	67·0	64·0–65·1
		59·88	3·88	5·26		

we are correlating differences in energy between the ground electronic state and excited electronic states of the same species. On an *a priori* basis it is not expected that there should be a universal constant for both these cases.

TABLE 6. CALCULATED TRANSITION ENERGIES (eV)

Band	H	Me	Cl	Br	MeO
1	1·539	1·577	1·579	1·573	1·574
2	2·438	2·308	2·290	2·263	2·289
3	2·795	2·934	2·914	2·891	2·764
4	2·931	2·932	2·931	2·932	2·922
5	2·958	2·994	3·007	2·989	3·001
6	3·006	3·042	3·046	3·039	3·049
7	3·013	3·044	3·056	3·045	3·088
8	3·120	3·120	3·109	3·107	3·112
9	3·162	3·110	3·121	3·087	3·108
10	3·222	3·189	3·655	3·500	3·674
11	3·228	3·150	3·146	3·097	3·134
12	3·491	3·634	3·611	3·580	3·667
13	3·827	3·662	3·643	3·622	3·637

TABLE 7. BAND PARAMETERS FOR BENZAL-ANILINE

Band	Intensity ($I°$)	Position ($\nu°$)	Width parameter (δ)	Oscillator strength
1	484	28,911	1131	0·0042
2	6325	31,079	2626	0·1272
3	304	33,137	1304	0·0030
4	523	34,389	918	0·0037
5	10,794	37,396	4088	0·3379
6	8167	38,699	2985	0·1867
7	276	39,640	1055	0·0022
8	438	40,767	1043	0·0035
9	909	42,133	825	0·0057
10	1258	42,426	608	0·0058
11	6917	44,112	1724	0·0913
12	1264	45,489	639	0·0062
13	30,993	51,416	5614	1·3322

TABLE 8. BAND PARAMETERS FOR BENZAL-*p*-TOLUIDINE

Band	Intensity ($I°$)	Position ($\nu°$)	Width parameter	Oscillator strength
1	694	28,818	981	0·0052
2	9217	30,763	2692	0·1900
4	520	33,100	1286	0·0051
3	534	34,453	923	0·0038
5	11,561	36,956	3633	0·3216
6	7752	39,015	3408	0·2023
7	488	38,496	1026	0·0038
9	1246	41,641	469	0·0045
8	67	43,244	1539	0·0008
11	11,887	43,698	2417	0·2200
10	986	45,032	736	0·0056
12	874	47,659	497	0·0033
13	41,881	51,083	4015	1·2876

The numerical data from these calculations which form the basis of our conclusions have been included in Tables 5–11.

Table 9. Band parameters for benzal-*p*Cl-aniline

Band	Intensity (I°)	Position (ν°)	Width parameter	Oscillator strength
1	455	28,945	1094	0·0038
2	8502	30,835	2746	0·1788
3	88	33,809	746	0·0005
4	403	34,555	898	0·0028
5	11,659	36,753	3754	0·3352
6	8957	38,992	3189	0·2187
7	845	40,262	817	0·0053
8	931	40,922	1114	0·0079
9	1273	41,907	616	0·0060
11	10,506	43,772	2028	0·1632
12	1123	45,192	902	0·0078
13	34,937	51,594	5005	1·3388

Table 10. Band parameters for benzal-*p*Br-aniline

Band	Intensity (*I*°)	Position (ν°)	Width parameter	Oscillator strength
1	946	38,978	1174	0·0085
2	11,229	31,002	2791	0·1400
3	781	34,188	1173	0·0070
4	479	34,882	1207	0·0044
5	12,726	36,849	3502	0·3413
6	11,806	38,664	3185	0·2879
7	427	40,697	1146	0·0037
9	1051	41,796	593	0·0048
11	9564	43,795	2010	0·1472
8	692	44,315	990	0·0052
10	348	45,120	649	0·0017
12	742	45,269	599	0·0034
13	34,957	51,457	5577	1·4927

Table 11. Band parameters for benzal-*p*-anisidine

Band	Intensity (*I*°)	Position (ν°)	Width parameter	Oscillator strength
1	901	28,188	1016	0·0070
2	10,129	29,947	2598	0·2015
3	590	33,449	931	0·0042
4	360	34,543	547	0·0015
5	8595	35,887	3432	0·2259
6	8897	39,114	3724	0·2537
7	471	38,154	923	0·0033
9	432	38,919	571	0·0019
8	346	42,764	690	0·0018
11	12,578	43,344	2720	0·2619
13	44,509	50,550	4520	1·5406

EXPERIMENTAL

Reagents. Fisher reagent grade benzaldehyde was redistilled under N_2 atm in small portions as required. The fraction boiling 177–180° was collected and stored in a stained glass container under N_2. British Drug Houses reagent grade aniline was redistilled over powdered Zn and the fraction boiling 182–185° was collected. Reagent grade *p*-*X*-aniline compounds were recrystallized from 95% EtOH, and their m.p. taken. The observed m.ps. were in agreement with reported values.

Preparation of benzal-p-X-*aniline compounds.* Equimolar portions of *p*-X-aniline and freshly distilled benzaldehyde were mixed and warmed to form a clear soln, (*p*-Me heated to 120° for 3 hr, *p*-Br heated to 100° for 10 min). The solns were then cooled and filtered. The resultant crystals were washed with an ice cold soln of two parts EtOH and three parts distilled water, then dissolved in hot EtOH. The product was recrystallized several times from 95% EtOH, and then analyzed for C, H and N content, and for m.p. The characteristics of these compounds are tabulated in Table 5.

UV spectra of benzal-p-X-*aniline.* The UV spectra of the compounds were recorded on a Unicam SP.800 Spectrophotometer calibrated linearly in wavenumbers. The intensity was recorded over the range 15,000–47,000 cm^{-1} for concentrations 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} moles/li. Spectra were taken in heptane using Matheson Coleman and Bell Spectroquality Reagent as supplied.

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