bands of NCSCN and NCSeCN. The antisymmetric $C\equiv N$ stretching frequencies in these analogs are 2179 cm^{-1} in NCSCN;[22] and 2178 cm^{-1} in NCSeCN.[23]

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(22) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1731 (1963).

(23) E. E. Aynsley, N. N. Greenwood, and M. J. Sprague, *J. Chem. Soc.*, 704 (1964).

On the Correlation between Structure and Dipole Moments in the Excited States of Substituted Benzenes[1]

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Abstract: The results of several recent high resolution spectroscopic investigations which measure dipole moments and structural parameters in the first excited $\pi^* \leftarrow \pi$ states of several substituted benzenes (phenol, aniline, *p*-fluorophenol, and *p*-fluoroaniline) are examined. The observed correlation between structure and moment allows us to make some definite observations as to the nature of intramolecular charge transfer on excitation, and this in turn allows a careful examination of various theoretical models for electronic structure in excited states.

Recent advances in the technology of high resolution optical spectroscopy coupled with increasing availability of computational techniques for spectral analysis have made possible determination of properties of molecules in excited electronic states to a high degree of accuracy. Spectral studies of polyatomic molecules in the gas phase under increasing resolution have revealed in numerous cases spectra rich in fine structure arising from transitions between individual rotational levels of the ground state to corresponding levels in the excited electronic state.[2] Just as the rotational energy levels deduced from microwave spectroscopy provide detailed and accurate information concerning molecular moments of inertia (and thereby bond lengths and bond angles) in the ground states, studies of the rotational fine structure of electronic spectra lead to accurate structural parameters of molecules in excited electronic states. Even for rather large molecules (*i.e.*, naphthalene, indole), though the spectra are complex, computers have enabled rotational analyses to be carried out.

The application of an external electric field (Stark effect) to polar molecules in the gas phase removes the spatial degeneracy (since all directions in space are no longer energetically equivalent) resulting in a splitting of observed rotational lines. This splitting is proportional to the difference in dipole moment between the two electronic states, and its measure allows accurate determination of dipole moments in excited electronic states.[3] The dipole moment is a sensitive measure of the electron density and consequently has been of inestimable value in understanding chemical properties of molecules in ground electronic states. It is thus expected that such measurements will be similarly helpful in understanding the nature of excited states.

From a chemical standpoint the actual values of various measured parameters sometimes are not as valuable as their relation to each other or their comparative values in a series of chemically related compounds. Such correlations are often quite valuable in understanding substituent effects, trends in reactivity or stability, and numerous other important properties, not to mention their predictive value.

An additional by-product of the computer age is the increasing availability of calculated wave functions for molecules in both ground and excited states. It is therefore also valuable to examine their relative ability to provide accurate predictive information concerning molecular properties.

It is the purpose of this paper to bring together results of several measurements of excited state structural parameters and dipole moments in a series of substituted benzenes. The observed correlation between structure and moment allows us to make some definite observations as to the nature of intramolecular charge transfer on excitation, and this in turn allows a careful examination of various theoretical models for electronic structure in excited states.

Experimental Results and Their Relationships

Rotational analyses of the lowest lying singlet $\pi^* \leftarrow \pi$ transitions ($B_2 \leftarrow A_1$) of aniline, phenol, *p*-fluoroaniline, and *p*-fluorophenol have recently been carried out by Christoffersen, Hollas, and Kirby.[4] The 0–0 vibrational bands were analyzed in each case. The resulting changes in rotational constants are listed in Table I. Although it is impossible to extract specific bond lengths and angles from rotational constants without extensive isotopic studies, it is possible to make some

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(1) Supported by NSF Grant No. GP 11530.

(2) J. M. Hollas, *Spectrochim. Acta*, **22**, 81 (1964); K. K. Innes and J. E. Parkin, *J. Mol. Spectrosc.*, **21**, 66 (1965); J. R. Lombardi, W. Klemperer, H. Basch, M. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **51**, 33 (1969); A. Mani and J. R. Lombardi, *J. Mol. Spectrosc.*, **31**, 308 (1969).

(3) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **40**, 604 (1964); **45**, 52 (1966); D. E. Freeman, J. R. Lombardi, and W. Klemperer, *ibid.*, **45**, 58 (1966); J. R. Lombardi, D. Campbell, and W. Klemperer, *ibid.*, **46**, 3482 (1967); J. R. Lombardi, D. E. Freeman, and W. Klemperer, *ibid.*, **46**, 2746 (1967); J. R. Lombardi, *ibid.*, **48**, 348 (1968).

(4) (a) J. Christoffersen, J. M. Hollas, and G. H. Kirby, *Proc. Roy. Soc., Ser. A*, 307, 97 (1968); (b) *Mol. Phys.*, in press; (c) manuscript in preparation.

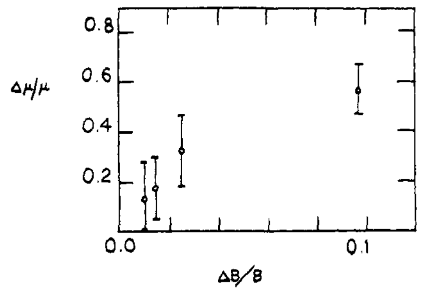

Figure 1. Correlation between fractional change in dipole moment and fractional change in B value on excitation ($\pi^* \leftarrow \pi$) for various substituted benzenes. In order of increasing $\Delta B/B$ these are phenol, *p*-fluorophenol, *p*-fluoroaniline, aniline.

important observations concerning these results. The most obvious regularity is that the change in B on excitation is positive for all observed cases. Since B is related to the moment of inertia about the b (short in-plane) axis

$$B = h^2/2I_b$$

an increased value for B indicates a decrease in the moment of inertia I_b on excitation. The moment of inertia about a particular axis is proportional to the sum of squares of atomic distances from that axis. Thus we may infer from the increase in B on excitation reduction of average bond length for bonds parallel to the a (long in-plane) axis.

Table I. Changes in Rotational B Value and Dipole Moment on Electronic Excitation ($\pi^* \leftarrow \pi$) in Several Substituted Benzenes

Molecule	Band, Å	ΔB, cm^{-1}	$\lvert\Delta\mu\rvert$, D
Phenol	2750	+0.00014	0.20 ± 0.2
Aniline	2938	+0.00136	0.85 ± 0.15
p-Fluorophenol	2847	+0.00073	0.44 ± 0.10
p-Fluoroaniline	3062	+0.00099	0.82 ± 0.09

Stark effect studies on the same absorption bands have recently been carried out in this laboratory,[5] and the resulting dipole moment changes are listed in Table I. Unfortunately, it was impossible to determine experimentally the *sign* of the change in moment on excitation. The decrease observed in pK_a values on excitation in phenol[6a] and *p*-fluorophenol[6b] indicates an *increase* of dipole moment on excitation (assuming the -OH to be positive with respect to the rest of the molecule). In addition, solvent shift studies on phenol and aniline[7] indicate an increase in this parameter on excitation. Thus, only for *p*-fluoroaniline is there lack of any indirect evidence for the sign of the moment change. We will assume for the sake of discussion that $\Delta\mu$ is positive in this case also.

We are then in a position to search for a relationship among the various experimental results. In Figure 1 is shown a plot of the values of $\Delta\mu/\mu$ against the values of $\Delta B/B$ for the four molecules in question. Although there is no theoretical justification for attempting to fit these results to a particular curve, there is no doubt that a strong correlation exists between changes in rotational constants and changes in dipole moments for these molecules. An extremely simple explanation of this correlation may be made by presupposing that a substantial contribution to the electronic structure of the excited state is made by a quinoid-like resonance structure. This structure attributes enhanced double bond character to these bonds parallel to the a axis, and simultaneously is strongly dipolar, and the correlation observed between structure and moment on excitation may be taken as evidence that this structure is more important in the excited state than the ground state and the results give us an indication of its relative importance within this series of molecules.

There is in fact additional structural information obtained from the rotational and vibrational analyses which confirms these trends. In phenol it is found that the barrier to the -OH torsional mode is larger in the excited state than the ground state by a factor of 3.5.[8] In aniline it is found that the angle between the bisector of the HNH angle and the CN axis is 39° in the ground state[9] while it is around 30° in the excited state.[4] Both of these structural data indicate increased participation of the p electrons of the substituent with the π system of the ring in the excited state.

The results presented in the previous section, with due regard to the assumptions made, suggest that the quinoid-like resonance structure makes a considerably enhanced contribution to the electronic structure of the excited state as compared with the ground state.

It should be first observed that the *para*-fluoro substitution does not drastically modify the dipole moment changes on excitation. For *para*-substituted compounds there are two possible dipolar structures which could be important in describing the excited state, one in which most of the charge is transferred from the substituent (-OH or -NH_2) into the ring, and the other in which most of the charge is transferred from the substituent to the fluorine. It may be argued that the latter must be an extremely small contributor to the excited state for two reasons. First if it were important it would result in drastically different dipole changes when comparing the *para*-fluoro substituted compounds with phenol and aniline. Secondly, the dipole moment of such a structure is on the order of 25 D owing to the large distance over which charge is transferred. The generally small dipole changes observed (in all cases $\Delta\mu < 1$ D) indicate that such a strongly dipolar contribution must be negligible. These qualitative observations are consistent with a calculation on *para*-substituted compounds carried out by Grinter and Heilbronner.[10]

Although no specific calculations are available for *p*-fluoroaniline and *p*-fluorophenol, several authors have attempted calculations on the excited states of phenol and aniline, and it is worthwhile to examine them more closely in the light of the experimental results. Several recent calculations[11-15] are listed as

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(5) J. R. Lombardi, *J. Chem. Phys.*, **50**, 3780 (1969); K. T. Huang and J. R. Lombardi, *ibid.*, **51**, 1228 (1969).

(6) (a) W. Bartok, P. Lucchesi, and N. Snider, *J. Amer. Chem. Soc.*, **84**, 1842 (1962); E. L. Wehry, *ibid.*, **89**, 41 (1967); (b) E. L. Wehry and L. B. Rodgers, *ibid.*, **87**, 4235 (1965).

(7) G. Weber, private communication.

(8) H. D. Bist, J. C. D. Brand, and D. R. Williams, *J. Mol. Spectrosc.*, **24**, 413 (1967).

(9) D. G. Lister and J. K. Tyler, *Chem. Commun.*, **6**, 152 (1966).

(10) R. Grinter and E. Heilbronner, *Helv. Chim. Acta*, **45**, 2496 (1962).

(11) H. Baba, *Bull. Chem. Soc. Jap.*, **34**, 76 (1961).

(12) K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

Table II. Results of Various Experimental and Theoretical Determinations of the Change in Dipole Moments in the First Excited $\pi^* \leftarrow \pi$ Transitions in Phenol and Aniline

Ref	Method	Phenol	Aniline
5	Experimental (optical Stark effect)	+0.20 ± 0.2	+0.85 ± 0.15
14	Experimental (solvent shift)	+5	
11	LCAO–MO–CI	+1.36	+3.61
12	Configuration interaction with charge transfer	+0.64	+2.31
13	Configuration analysis	+0.68	
14	Isoconjugate hydrocarbon		+7.6
15	Pariser–Parr SCF		+2.6

references of Table II. All these calculations were made only on the π-electron system, but since the transitions observed are $\pi^* \leftarrow \pi$ it may be legitimate to compare experimental changes in dipole moment with those obtained from the calculations. The listed calculations all involve adjusting various parameters to obtain a best fit to the excitation energies of the π electrons.

The earliest calculations were those of Baba[11] who used an LCAO–MO–CI technique. He reported the change in charge on the substituent upon excitation. Assuming the charge transfer is into the ring, we may use this to determine a predicted change in moment on excitation by simply multiplying by the linear distance from the substituent to the center of the ring. The resulting dipole changes are 1.36 and 3.61 D for phenol and aniline. It can be seen that these values overestimate the experimental results by more than a factor of 6, but do at least agree that the change for aniline is somewhat more than for phenol.

The calculations by Kimura and Nagakura[12] are basically of the configuration interaction type, describing the electronic states as linear combinations of benzene functions plus charge transfer functions formed by removing an electron from a substituent orbital and placing it in a benzene orbital. If one chooses the origin of a coordinate system in the center of the benzene ring, then this intermolecular charge transfer term is the only contributor to the *change* in dipole moment on excitation. The predicted change may then be calculated by standard quantum mechanical techniques. The results of this calculation are 0.64 and 2.31 D for phenol and aniline. These are somewhat closer to the experimental results than those of Baba[11] but are still too large by a factor of 3. In a later calculation on phenol Baba, Suzuki, and Takemura[13] use a technique they call configuration analysis. This technique is similar to that of Kimura and Nagakura,[12] in which a charge transfer configuration is explicitly included. The dipole moment change is then determined to be 0.68 D, in good agreement with the previous result.

Murrell[14] has used the isoconjugate hydrocarbon model for a determination in aniline. The result is 7.6 D, considerably worse than the previous calculations.

The only other calculation available is that by Labhart[15] using the Pariser–Parr SCF technique. He finds a value of 2.6 D for aniline, in good agreement with Kimura and Nagakura[12] but still somewhat larger than the experimental result.

All the calculations seem to agree that the change in moment for aniline should be larger than that for phenol, but all more or less overestimate considerably the actual change. The best results seem to be those that include a charge-transfer term explicitly. It is probable that any π-electron calculation is bound to overestimate the dipole moment change because it fails to take into account the polarization of the inner σ electrons by the π system.

Note also that the geometric changes (*e.g.*, shortening of bond lengths) on excitation have not been taken into account in the calculations. These could also be responsible for part of the dipolar changes. Several of the multicenter integrals in calculations depend strongly on geometry. It would be valuable to have some estimate as to the magnitude of this effect. This also points out the need for accurate measurements of dipole moment derivatives.

Also listed in Table II is the only other published experimental determination of an excited state dipole moment in aniline. The result is a reported change of +5 D on excitation. The technique used is that of observation of solvent shifts of the spectrum. This method must be termed unreliable for at least two reasons. In the first place one must guess the solvent cavity radius. Note that even if this could be done to ±30%, since the dipole moment is proportional to the cavity volume, a 30% error in radius becomes a 90% error in dipole moment. In addition the theory does not take into account the possibilities of nearby excited states. If another electronic state is nearby and has a nonzero transition moment with the observed state, *even if this nearby state is not itself observed spectrally*, it could drastically shift the spectrum, causing incorrect values of the dipole moment to be obtained. For example, a brief calculation shows that an excited state 2000 cm^{-1} from the observed state with a transition moment of 1 D could change the apparent dipole by 2–3 D at typical internal fields obtained in liquids. Hence, one should use considerable caution in using results of these experiments for diagnostic or predictive investigations.[16]

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(13) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, 50, 2078 (1969).

(14) J. N. Murrell, *Tetrahedron, Suppl.*, No. 2, 277 (1963).

(15) H. Labhart, comment following ref 14.

(16) NOTE ADDED IN PROOF: Additional confirmation of the correlation described in Figure 1 comes from an experiment recently completed in this laboratory on fluorobenzene. The measured change in *B* value and dipole moment add an additional point on the graph and in this case we also determine experimentally the *sign* of the change in moment. For further details see K.-T. Huang and J. R. Lombardi, *J. Chem. Phys.*, in press.