

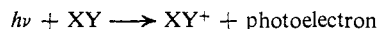
A Study of the Energy Levels in Benzene and Some Fluorobenzenes by Photoelectron Spectroscopy¹

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Contribution from the Chemistry Department, University of British Columbia, Vancouver, Canada. Received August 3, 1966

Abstract: The relatively new method of photoelectron spectroscopy has been used to measure the first and inner ionization potentials of benzene and four fluorine-substituted benzenes. Correlations between the higher levels in the fluorobenzenes are attempted using simple Hückel molecular orbital (HMO) theory and the assumption that the second level in benzene is π .

Photoelectron spectroscopy is simply an application of the photoelectric effect in the gas phase. In the reaction



conservation of momentum predicts that the photoelectron is endowed with virtually all the energy over and above that required to ionize XY. If $h\nu$ is known and the photoelectron kinetic energy determined, the ionization potential (IP) of XY may be deduced.

Since molecules as large as benzene possess many orbitals with different energies, the emitted photoelectrons will have quite a complex energy distribution. It is in the study of these inner energy levels, so intimately connected with molecular structure, that photoelectron spectroscopy demonstrates its utility.

The inner IP's provide the most direct experimental test of accuracy for the many theoretical calculations currently being applied to molecules such as benzene. However, studies of the nature of even the energies of the energy levels have been difficult to perform.

Traditional methods for IP measurement have been largely unsuccessful where inner levels are concerned, mainly because excitation and/or autoionization processes obscure those features which would indicate the IP.

The best literature values for benzene from electron impact³ and Rydberg series methods,⁴ as well as the previous photoelectron spectroscopic values by Turner,⁵ are shown in Table I, with the orbitals to which the potentials were thought to refer.

Table I. Previous Values for the IP's of Benzene and Their Suggested Origins (in ev)

| Electron impact ³ | Rydberg series ⁴ | Photoelectron spectroscopy ⁵ |
|------------------------------|-----------------------------|--|
| 9.21, π 9.7 | 9.248, $\pi(e_{2g})$ | 9.25, $\pi(e_{2g})$ |
| 10.4 (?) | | |
| 11.5, σ | 11.489, $\pi(a_{2u})$ | 11.49, $\pi(a_{2u})$ 12.19 (?) 13.67 |
| 14.3 | | 14.44 (?) |
| 15.5 | 16.84, σ_{cc} | 16.73 18.75 |

(1) Presented at the American Chemical Society Northwest Regional Meeting, June 16, 1966.

(2) 1966 Rhodes Scholar.

(3) R. E. Fox and W. M. Hickam, *J. Chem. Phys.*, **22**, 2059 (1954).

(4) M. F. El Sayed and M. Kasha, *ibid.*, **34**, 334 (1961).

(5) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

The highest level in benzene is generally assumed to be π . However, experimental studies using both Rydberg series⁴ and photoelectron methods,⁵ which designate the second level to be π (Table I), disagree with the various theoretical calculations⁶ which predict two or three σ levels between the two π levels. El Sayed and Kasha⁴ give spectroscopic evidence for their π MO assignment for the second level (there is only a small effect on the vibrational structure on deuteration, and the sharpness of the observed Rydberg series makes it hard to correlate with the σ ionization of paraffins). Turner⁵ points out that the separation of the 11.49- and 9.25-ev levels is 2.24 ev, in good agreement with estimates of the parameter β_0 calculated from Hückel molecular orbital (HMO) theory.

The purpose of this work was to experimentally determine the energy levels of benzene and a series of substituted fluorobenzenes so that the perturbing effect of substituted atoms may be examined. It was hoped that a systematic study of these levels would help to identify the energy levels in benzene more conclusively. The use of spherical grid energy analysis allows the recording of the photoelectron stopping curve directly instead of its differential, making it possible to compare the probabilities of ionization from the various orbitals. In addition, an attempt is made to correlate the higher levels in the compounds studied using simple HMO theory based on Kasha and Turner's assumption that the 11.5-ev level is π .

Experimental Details

A full description of the instrument is to appear elsewhere;⁷ however, we propose to give a few of the more pertinent details here.

Photons of wavelength 584 Å (21.21 ev) are generated by helium in a 2450-Mcps microwave discharge and are used to ionize sample gas at the center of a spherical grid system. The resulting photoelectrons are energy analyzed by means of a continuously variable retarding voltage on a spherical collector. The collector current is amplified by a Cary Model 31 vibrating reed electrometer and displayed on a strip chart recorder.

The spherical analyzer has a decided advantage over the more conventional cylindrical design since very few photoelectrons are ejected at 90° to the incident light beam. In fact, the angular distribution is thought to vary as $\cos^2 \theta$. In the spherical case the retarding field is always normal to the photoelectron trajectory and a much cleaner energy spectrum is obtained.

(6) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (b) J. M. Shulman and J. W. Moskowitz, *ibid.*, **43**, 3287 (1965); (c) M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2373 (1966).

(7) D. C. Frost, C. A. McDowell, and D. A. Vroom, to be published.

Table II. Ionization Potentials of Benzene and Some Fluorobenzenes (in ev)

| Benzene | Monofluorobenzene | 1,4-Difluorobenzene | 1,2,4-Tri-fluorobenzene | Hexafluorobenzene |
|----------------|-------------------|---------------------|-------------------------|-------------------|
| 9.25 ± 0.02 | 9.21 ± 0.04 | 9.15 ± 0.06 | 9.30 ± 0.05 | 9.88 ± 0.05 |
| 11.51 ± 0.04 | 9.87 ± 0.07 | 10.04 ± 0.08 | 10.05 ± 0.04 | 11.12 ± 0.06 |
| 13.88 ± 0.04 | 11.83 ± 0.07 | 12.16 ± 0.06 | 12.26 ± 0.04 | 11.64 ± 0.06 |
| (14.87 ± 0.06) | 12.98 ± 0.08 | 13.55 ± 0.06 | 12.93 ± 0.05 | 12.71 ± 0.06 |
| (15.54 ± 0.06) | 13.89 ± 0.07 | 14.24 ± 0.06 | 13.64 ± 0.05 | 13.75 ± 0.07 |
| 16.84 ± 0.05 | 14.55 ± 0.09 | 15.01 ± 0.1 | 14.35 ± 0.06 | (13.93 ± 0.07) |
| 18.22 ± 0.08 | 16.24 ± 0.08 | (15.44 ± 0.1) | 15.26 ± 0.08 | 14.64 ± 0.05 |
| (18.82 ± 0.1) | 17.77 ± 0.09 | (16.79 ± 0.1) | (15.93 ± 0.1) | 15.73 ± 0.07 |
| 20.26 ± 0.08 | (19.02 ± 0.09) | 17.12 ± 0.1 | (16.92 ± 0.1) | 16.16 ± 0.1 |
| | (19.55 ± 0.2) | 17.93 ± 0.1 | 17.07 ± 0.08 | 17.42 ± 0.07 |
| | 20.69 ± 0.1 | 19.74 ± 0.1 | 17.92 ± 0.08 | 18.15 ± 0.08 |
| | | (20.3 ± 0.1) | 20.5 ± 0.2 | (19.5 ± 0.3) |

The reagent grade benzene, monofluorobenzene (Peninsular Chemical Research Inc.), 1,4-difluorobenzene, 1,2,4-trifluorobenzene, and hexafluorobenzene (I.C.I. Ltd., Widnes, England) were, used without further purification after mass spectral analysis failed to detect any impurity which could cause ambiguity in the photoelectron stopping curves.

In a subsidiary experiment for each gas, a small quantity of argon is admitted simultaneously with the sample and a composite stopping curve obtained. Since the IP of argon is well known (15.77 ev), the sharp argon threshold serves to calibrate the energy scale.

Experimental Results

The photoelectron stopping curves for benzene, monofluorobenzene, 1,4-difluorobenzene, 1,2,4-trifluorobenzene, and hexafluorobenzene are shown in Figure 1. Well-defined breaks are clearly present in all the curves; however, the existence of those denoted by dotted lines is somewhat uncertain and their energies are placed in parentheses in Table II, wherein all our energy level data are collected. The quoted errors are uncertainty limits estimated from the curves.

Discussion

Three of our IP's for benzene are in excellent agreement with the three available Rydberg series values. Turner's 16.13-ev value would therefore appear to be slightly low. Although the instrument is capable of easily resolving the argon ionic $^2P_{3/2} - ^2P_{1/2}$ doublet (separation 0.18 ev), the ill-defined nature of the breaks in the stopping curves for large molecules like the ones studied here (probably due to vibrational excitations) makes it difficult to resolve electronic levels separated by less than about 0.2 ev.

When the heights of the steps in the photoelectron stopping curves are used to estimate the relative probability of ionization from the various orbitals, it must be remembered that the cross section for photoionization usually increases as $h\nu - \text{IP}$ decreases, and the relative probabilities we measure are those pertaining at 21.21 ev. However, the relative probabilities are not expected to differ by more than a factor of 2 within the energy range studied.

HMO Calculations

It will now be shown that, if the assumption of Kasha and Turner regarding the 11.5-ev level in benzene is correct, it should be possible to predict the π levels in the substituted fluorobenzenes and thus apply the HMO theory of π electrons to these levels.

If the 11.5-ev level in benzene is π , then all the lower levels must be σ . Since we expect the inductive effects

of the substituted fluorine atoms to lower the energy of the σ orbitals, we can draw an upper limit for the energy of the σ orbitals in the fluorobenzenes. As shown by the dotted line in Figure 2 this limit starts at the 13.88-ev

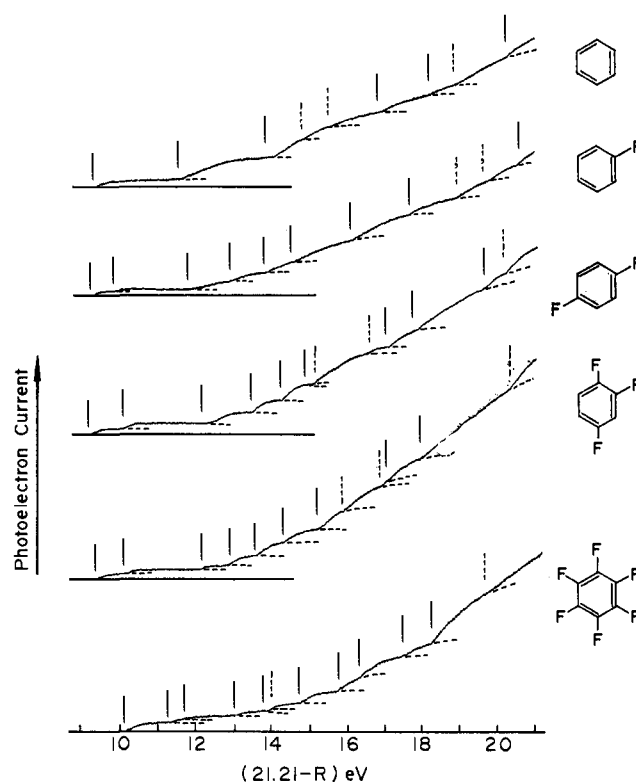


Figure 1. Photoelectron stopping curves for benzene, C_6H_5F , 1,4- $C_6H_4F_2$, 1,2,4- $C_6H_3F_3$, and C_6F_6 . The breaks considered to be uncertain are indicated by dotted lines.

level in benzene and connects levels which are progressively depressed in energy as F atoms are substituted. It can be seen that in no case are there more levels above this line than the number of energetically different π levels present in each compound (*i.e.*, four in C_6H_5F , five in $C_6H_4F_2$, six in both 1,2,4- $C_6H_3F_3$ and C_6F_6).

If this reasoning is correct all levels above this line will be π , and it should be possible to apply the HMO theory which in its simple form is the oldest and most empirical of the molecular orbital theories. There are many accounts of the theory (see, for example,

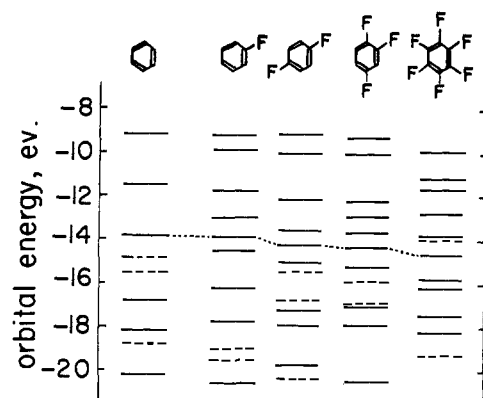


Figure 2. Energy level diagram for benzene and four fluorine-substituted benzenes.

Coulson⁸ and Streitwieser⁹), and it has been used extensively with varied success in correlating properties of molecules containing π electron systems. The theory applies only to π orbitals, and the energy calculations do not yield the energy directly but give it in terms of undetermined parameters α_0 and β_0 . To account for the presence of a substituent atom (X, such as fluorine) in the molecule, appropriate changes are made in the α and β associated with each atom and bond. These changes are incorporated in units of the standard α_0 and β_0 of benzene using the definitions

$$\alpha_X = \alpha_0 + h_X\beta_0$$

$$\beta_{CX} = k_{CX}\beta_0$$

In addition an auxiliary inductive parameter (AIP) is often used to account for the inductive effect of X on an adjacent carbon. Thus, for the C_α -X group $h_{C_\alpha} = \delta h_X$ with δ usually taken as 0.1.

Diagonalization of the Hückel matrix yields the m_i in the equation

$$E_i = a + m_i\beta_0$$

where E_i is the energy of the i th π orbital. Thus the correlation between the Hückel theory and experimental results involves plotting the experimental energies, *i.e.*, the ionization potentials, against m_i , which would ideally yield a straight line of slope β_0 .

Since the literature values differ considerably, the h and k for fluorine were calculated by fitting them to the first four energy levels on monofluorobenzene. It can be seen (Table III) that the resultant value of k is in agreement with the two previous estimates and that the best fit h agrees more closely with I'Haya's¹⁰ than with Streitwieser's value. These values were then used in Hückel calculations (using an AIP of $0.1h$ throughout) for the three remaining fluorobenzenes.

Table III. The Hückel MO h and k Parameters for Benzene

| | I'Haya ¹⁰ | Streitwieser ⁹ | This work |
|-----|----------------------|---------------------------|-----------|
| h | 1.5-2.1 | 3 | 1.65 |
| k | 0.5-0.7 | 0.7 | 0.65 |

(8) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961.

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

(10) Y. I'Haya, *J. Am. Chem. Soc.*, **81**, 6120 (1959).

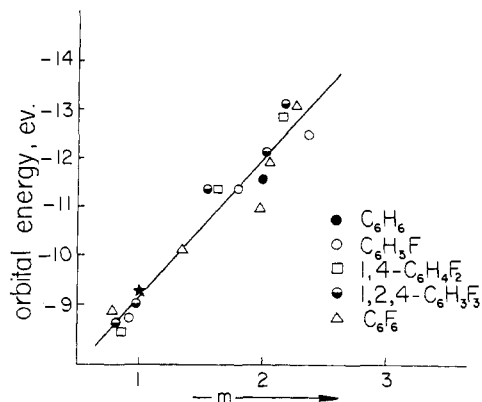


Figure 3. Relationship between orbital energy and the Hückel m for those levels we propose to be π . The energy scale for each fluorobenzene is adjusted to make the $m = 1.0$ energy coincide with the 9.25-ev value in benzene, indicated by a star. Only C_6H_6 , C_6H_5F , and 1,4- $C_6H_4F_2$ actually have energy levels at $m = 1.0$; the Hückel matrix yields no $m = 1.0$ level for the other two compounds.

The degree to which the HMO results correlate with the experimental levels as expressed by the correlation coefficients for the IP *vs.* m plots is shown in Table IV and is seen to be very good by HMO standards. The values of β_0 obtained for each molecule all fall within the range of those calculated from other published correlations. α_0 was found to vary considerably among the compounds (the levels corresponding to $m = 1.0$ in C_6H_6 , C_6H_5F , and 1,4- $C_6H_4F_2$ have energies of 9.25, 9.87, and 10.04 ev, respectively). For this reason Figure 3, which shows the rather high degree of correlation between the levels in all five molecules, has been plotted after shifting the energy scales for each molecule to make the $m = 1.0$ levels correspond to the same energy (in particular to the 9.25-ev value in benzene, starred in the figure).

Table IV. Results of Correlations between IP and m for Benzene and Some Fluorinated Benzenes

| | Slope (β_0) with rms error | Correlation coefficient |
|------------------------|--|----------------------------|
| Benzene | 2.26 | |
| Monofluorobenzene | 2.59 ± 0.15 | 0.993 |
| 1,4-Difluorobenzene | 3.28 ± 0.18 | 0.993 |
| 1,2,4-Trifluorobenzene | 2.19 ± 0.33 | 0.934 |
| Hexafluorobenzene | 2.33 ± 0.30 | 0.996 |

It must be remembered that two adjustable parameters (h and k) were used to give the best correlation among the C_6H_5F levels, and it is difficult to tell if the resultant good correlations with the other levels were simply fortuitous. There have been no comparable Hückel calculations in the literature, presumably owing to lack of experimental data on inner energy levels.

Hückel correlations based on the alternate assumption⁶ of $\pi \sigma \sigma \sigma \pi \sigma \dots$ ordering in benzene were not possible because of the difficulty in assigning π levels in the fluorobenzenes.

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An Investigation into the Source of C≡N Vibrational Frequency Shifts

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Abstract: The results of normal coordinate analyses and molecular orbital calculations are utilized to explain the increase in C≡N vibrational frequency when either the carbon or nitrogen atom acts as a Lewis base. The molecules included in this study are CN⁻, CH₃CN, CH₃NC, ClCN, BrCN, ICN, and HCN. Detailed comparisons are made for CN⁻ and HCN, and CH₃CN and CH₃NC.

In a recent report¹ the utility of an approximate LCAO-MO method was demonstrated in augmenting normal coordinate analyses in a study of the bonding in acetonitrile and its adducts. The primary question there was the source of the increase in energy of the "C≡N" normal mode upon coordinate bond formation by the N "lone pair." We wish to report analogous calculations here for the C and N lone pairs of CN⁻ which are in agreement with the earlier computations and which substantiate the earlier interpretation.

Calculational Methods

The molecular orbital calculations were carried out in a manner previously described.¹ Briefly, a modification of the extended Hückel method was used with Slater exponents and valence-state ionization potentials² for neutral atoms as initial values. Off-diagonal elements of the *H* matrix were calculated from the overlap integrals and the arithmetic mean of the diagonal elements using a proportionality constant of 1.75.³ (The use of the geometric mean does not alter any of our conclusions.) Valence-state ionization energies were adjusted for atom charge by 2.0 eV/atomic unit and the Slater exponents by Slater's formula.⁴ The calculations were iterative with respect to self-consistent atom charges to within 0.01 charge unit.

The results of these calculations have been analyzed *via* the Mulliken overlap population procedure⁵ to yield, for example, the overlap populations themselves and the overlap energies (Ω). The magnitude of Ω_{ij} for a pair of interacting atomic orbitals (X_i, X_j) depends on the definition⁵ of β in

$$\Omega_{ij} = n(i,j)\beta_{ij}/S_{ij}$$

For $\beta_{ij} \equiv H_{ij}$ the overlap energies are larger, of course,

- (1) K. F. Purcell and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 919 (1966).
- (2) (a) J. Hinze and H. H. Jaffé, *ibid.*, **84**, 540 (1962); (b) *J. Phys. Chem.*, **67**, 1510 (1963).
- (3) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397, 2745; **40**, 2474, 2480 (1964).
- (4) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).
- (5) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

than for $\beta_{ij} \equiv H_{ij} - S_{ij}\bar{\alpha}$. Qualitatively our results do not depend upon which definition we use; only the magnitudes of the numbers differ. Since the definition given by Mulliken bears a closer relationship to what one thinks of when one uses the term "covalent energy," we report only those values of Ω calculated from the latter definition. Finally these energy terms are analyzed at the "subtotal" and "total" levels.

Results and Discussion

The results of our calculations in terms of total overlap energies and overlap populations are presented, along with other pertinent data, in Table I and in terms of subtotal energies in Table II. All of the neutral molecules may be thought of as arising from CN⁻ by coordination of X⁺ through the carbon or nitrogen lone pair. In every instance an increase in the C≡N force constant is observed which is in part¹ responsible for the higher C≡N vibrational frequencies relative to CN⁻. This behavior is quite common for the cyano group where back-donation from an electron-rich acceptor is not possible, but is quite unusual for coordination at a multiply bound donor atom site. In the case of doubly and singly bound atoms, polarization of π and σ molecular orbitals appears to be the major effect and bond weakening occurs.

Table I

| Compound | $-\Omega_{CN}$, ev | F_{CN} , mdynes/A | n_{CN} | R_{CN}^e |
|--------------------|---------------------|------------------------|----------|------------|
| CN ⁻ | 19.628 | 16.4 ^a | 1.805 | 1.140 |
| CH ₃ NC | 19.661 | 16.7 ^b | 1.715 | 1.167 |
| BrCN | 19.738 | 17.8 ^c | 1.718 | 1.160 |
| ICN | 19.954 | 17.9 ^c | 1.754 | 1.159 |
| CH ₃ CN | 20.350 | 18.1 ^b | 1.759 | 1.157 |
| ClCN | 20.361 | 17.6 ^c | 1.730 | 1.163 |
| HCN | 20.939 | 18.7 ^d | 1.809 | 1.156 |

- ^a This work. ^b J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964).
^c E. E. Aynsley and R. Little, *ibid.*, **18**, 667 (1962). ^d H. C. Allen, Jr., E. D. Tidwell, and E. K. Plyler, *J. Chem. Phys.*, **25**, 302 (1956).
^e L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.