Photoelectron Spectra of Molecules
Part 5.1—Polycyclic Aromatic Hydrocarbons

BY M. J. S. DEWAR AND D. W. GOODMAN *

Dept. of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

Received 6th April, 1972

A retarding potential cylindrical grid photoelectron spectrometer has been constructed capable of operation up to 300°C. Spectra have been measured for a number of polycyclic benzenoid hydrocarbons. The ionization potentials are compared with those given by other spectroscopic methods and electron impact, with estimates from polarographic oxidation potentials and charge transfer spectra of π molecular complexes, and with values calculated by a SCF MO π approximation. All these alternative procedures lead to significant errors.

Although the ionization potentials of aromatic molecules are vital to the interpretation of the spectra and structures of π molecular complexes, few reliable values have as yet been reported. It is well recognized that ionization potentials derived by electron impact methods are liable to errors of at least 0.5 eV while photo-ionization and photoelectron studies have been mostly limited to compounds with sufficient vapour pressure at room temperature to give detectable spectra.

Dewar, Haselbach, and Worley 2 recently reported measurements of ionization potentials for a number of aromatic compounds using a spectrometer that could be operated at temperatures up to 150°C. This enabled them to record spectra for several compounds that could not be studied at room temperature. We have now modified the spectrometer so that it can be operated at temperatures up to 300°C and have consequently been able to extend the measurements to a number of even less volatile hydrocarbons.

The spectrometer is of the cylindrical grid retarding potential type devised by Al-Joubury and Turner.3 Such spectrometers suffer from low resolution but this is not important in the present connection. The main interest here lies in the values of the first ionization potentials and these are reproduced with sufficient accuracy (±0.02 eV) by grid-type instruments. Retarding potential spectrometers offer advantages for high temperature operation since it is relatively simple to heat the entire spectrometer in a thermostatted oven. Most attempts to use deflection-type spectrometers at high temperatures seem to have been based on heated ionization chambers, the spectrometer itself being at room temperature. Here complications may arise from condensation of nonvolatile materials on the electrodes.

The resolution of grid-type spectrometers can be improved by using spherical grids,4 or by replacing the inner grid by a stack of annular plates.5 We tried the later modification and were indeed able to obtain well resolved (±40 meV) spectra for a number of small molecules. Unfortunately, however, the sensitivity proved inadequate for the large aromatic systems since the ionization currents fell very rapidly with increasing molecular size. The measurements reported here were therefore carried out with the original cylindrical grids.

* National Science Foundation Predoctoral Trainee.

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The original spectrometer has been described elsewhere. It followed the original design of Al-Joboury and Turner except in that the electrodes were mounted on lead-through glass insulators set in a massive brass-plate which was grounded to act as a guard ring. It was thought that this expedient would allow the spectrometer to be heated, the grounded base-plate preventing leakage between the electrodes at temperatures where glass begins to conduct. In practice, however, it proved impossible to operate at temperatures higher than 150°C due to microphonic effects and the onset of large anode currents. We found that these currents were due not to leakage between the electrodes but to thermoelectric potentials between them set up when the resistance of the insulators begins to fall. The problem was solved by using sapphire lead-through insulators. The microphonic effects were controlled by mounting the spectrometer on shock-absorbing supports and bracing the electrodes with sapphire insulators. The instrument now operates satisfactorily up to 300°C, ample for the present purpose.

The materials studied were commercial samples, purified and degassed by vacuum sublimation before use. Since no pressure gauges are available that can operate at high temperatures in the micron region, the pressure of the sample could not be measured. Measurements were therefore carried out with the sample tube at progressively increasing temperatures until a satisfactory spectrum was obtained, the spectrometer being held at a considerably higher temperature to prevent condensation. Published vapour pressure data suggest that the results reported here were obtained at 0.05–0.1 Torr.

CALCULATION OF IONIZATION POTENTIALS

As a check on the experimental values, ionization potentials were calculated by two variants of a semiempirical SCF MO method developed here. These are based on the Hückel σ, π approximation, the SCF calculation referring only to the π electrons. The procedure here is essentially that of Pople, parameterized to give good estimates of ground state properties. Previous studies had shown this to give very good estimates of π ionization potentials.

The two theoretical treatments differ in the procedure used to estimate the one-electron core resonance integrals. In the first, these are found by the thermocycle method of Dewar and Schmeising; in the second, by the Mulliken approximation.

The parameters used in the first procedure were those of Dewar and de Llano. In each case the first ionization potentials were estimated both from Koopmans' Theorem (which also gave estimates of the higher ionizations) and by difference between the energies calculated for each molecule and the corresponding ion. The former values should be estimates of vertical ionization potentials while the latter should refer to adiabatic ionization and so be more directly comparable with the values measured here.

RESULTS AND DISCUSSION

Fig. 1 shows a typical spectrum. The first break, corresponding to the first ionization potential, is very well defined, being usually reproducible to 0.01 eV. The values for the higher ionization potentials are less reliable, due to the base line drift inevitable in spectrometers of this type. However, in cases where the higher π ionization potentials have been measured using high resolution spectrometers, the results agree quite well with those given by the present instrument.

Table 1 shows values for the first ionization potentials measured here, together with those calculated by the π MO procedure. Values for benzene, naphthalene, azulene, biphenyl and phenanthrene are included for reference, the photoelectron values being those reported in part 3.

Table 1 also lists ionization potentials measured by electron impact (EI), together with estimates from polarographic oxidation studies (PO) and charge transfer spectra of π molecular complexes (CT). The only compound of the series that has been
studied by other accurate procedures is anthracene; the ionization potentials for
this found from Rydberg series (7.41 eV) and photoionization spectroscopy (7.5 eV)\textsuperscript{12}
agree well with ours.

\begin{center}
\begin{tikzpicture}
\begin{axis}[
width=\textwidth, height=\textwidth,
xmin=-14, xmax=0,
ymin=0, ymax=5.5,
no markers, thick
]
\addplot table [col sep=comma] {\text{data.csv}};
\addplot [black, only marks, mark size=1pt] table [col sep=comma] {data.csv};
\end{axis}
\end{tikzpicture}
\end{center}

\text{retarding potential = photoelectron kinetic energy/V}

\text{Fig. 1.-Photoelectron spectrum of anthracene. Excitation source was 584 Å (21.21 eV) resonance}
\text{line of helium.}

The electron impact values are, as usual, unreliable, being too high by amounts
varying erratically from 0.1-0.35 eV. Since the present procedure gives much more
accurate results much more quickly, using cheap and simple equipment, and since it
also gives estimates of the higher ionization potentials as well, there seems little
future scope for the electron impact method in this area.

The agreement between our values and those estimated from charge transfer
spectra is generally good though there are some quite serious exceptions (triphenylene
and the terphenyls). Such deviations are not surprising because the coulombic
energy of the ion pair produced by the CT transition must vary significantly from
one donor to another. Similar considerations apply to correlations of oxidation
potentials in solution with ionization potentials in the gas phase, the former being
subject to erratic variations due to differences in the heat of solvation of the cation-
radicals derived by oxidation of the aromatic substrates.

The calculated ionization potentials agree reasonably well with the experimental
values, the agreement being better for the adiabatic values than for those derived from
Koopman's Theorem and better for the calculations based on the Mulliken expression
for the resonance integrals than those using the thermocycle approximation. Since
the values for Koopman's Theorem should refer to vertical ionization, it is satisfac-
tory that the adiabatic values agree better with ours. Fig. 2 shows a plot of the
measured first ionization potentials from table 1 against the adiabatic values based
on the Mulliken approximation. The points all lie within 0.2 eV of a straight line
Table 1.—First ionization potentials for unsaturated polycyclic hydrocarbons

<table>
<thead>
<tr>
<th>molecule</th>
<th>PS (^b)</th>
<th>CT (^b)</th>
<th>PO (^b)</th>
<th>EI (^b)</th>
<th>(n^a)</th>
<th>(n^d)</th>
<th>(n^e)</th>
<th>(n^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>9.24 (^g)</td>
<td>9.21 (^h)</td>
<td>9.01 (^l)</td>
<td>9.52 (^l)</td>
<td>9.37</td>
<td>9.22</td>
<td>9.37</td>
<td>9.21</td>
</tr>
<tr>
<td>naphthalene</td>
<td>8.11 (^g)</td>
<td>8.10 (^h)</td>
<td>8.12 (^l)</td>
<td>8.26 (^m)</td>
<td>8.57</td>
<td>8.30</td>
<td>8.54</td>
<td>8.23</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>7.91 (^g)</td>
<td>8.09 (^h)</td>
<td>8.03 (^k)</td>
<td>8.03 (^n)</td>
<td>8.45</td>
<td>8.10</td>
<td>8.43</td>
<td>8.04</td>
</tr>
<tr>
<td>azulene</td>
<td>7.43 (^g)</td>
<td>7.72 (^o)</td>
<td>7.79</td>
<td>7.53</td>
<td>7.81</td>
<td>7.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fluoranthrene</td>
<td>7.80 (^g)</td>
<td>8.36</td>
<td>8.04</td>
<td>8.34</td>
<td>7.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>8.02 (^g)</td>
<td>8.71</td>
<td>8.43</td>
<td>8.69</td>
<td>8.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>biphenyl</td>
<td>8.23 (^g)</td>
<td>8.46 (^l)</td>
<td>8.96 (^p)</td>
<td>8.63</td>
<td>8.30</td>
<td>8.63</td>
<td>8.27</td>
<td></td>
</tr>
<tr>
<td>anthracene</td>
<td>7.47</td>
<td>7.37 (^h)</td>
<td>7.43 (^k)</td>
<td>7.55 (^n)</td>
<td>8.00</td>
<td>7.72</td>
<td>7.97</td>
<td>7.62</td>
</tr>
<tr>
<td>pyrene</td>
<td>7.45</td>
<td>7.55 (^h)</td>
<td>7.54 (^k)</td>
<td>7.72 (^q)</td>
<td>7.97</td>
<td>7.71</td>
<td>7.95</td>
<td>7.63</td>
</tr>
<tr>
<td>perylene</td>
<td>6.90</td>
<td>7.03 (^h)</td>
<td></td>
<td></td>
<td>7.76</td>
<td>7.44</td>
<td>7.72</td>
<td>7.35</td>
</tr>
<tr>
<td>triphenylene</td>
<td>7.84</td>
<td>8.09 (^h)</td>
<td>8.10 (^k)</td>
<td>8.19 (^q)</td>
<td>8.46</td>
<td>8.12</td>
<td>8.45</td>
<td>8.10</td>
</tr>
<tr>
<td>1,2-benzanthracene</td>
<td>7.56</td>
<td>7.45 (^h)</td>
<td>7.57 (^k)</td>
<td></td>
<td>8.00</td>
<td>7.73</td>
<td>8.04</td>
<td>7.66</td>
</tr>
<tr>
<td>3,4-benzotetraphene</td>
<td>7.35</td>
<td></td>
<td></td>
<td></td>
<td>7.90</td>
<td>7.57</td>
<td>7.88</td>
<td>7.47</td>
</tr>
<tr>
<td>1,2-benzopyrene</td>
<td>7.39</td>
<td>7.56 (^h)</td>
<td></td>
<td></td>
<td>8.04</td>
<td>7.76</td>
<td>8.03</td>
<td>7.71</td>
</tr>
<tr>
<td>p-terphenyl</td>
<td>7.78</td>
<td>8.29 (^l)</td>
<td></td>
<td></td>
<td>8.34</td>
<td>7.95</td>
<td>8.33</td>
<td>7.93</td>
</tr>
<tr>
<td>o-terphenyl</td>
<td>7.99</td>
<td>8.43 (^l)</td>
<td></td>
<td></td>
<td>8.40</td>
<td>7.91</td>
<td>8.40</td>
<td>8.00</td>
</tr>
<tr>
<td>m-terphenyl</td>
<td>8.01</td>
<td></td>
<td></td>
<td></td>
<td>8.51</td>
<td>8.24</td>
<td>8.51</td>
<td>8.21</td>
</tr>
<tr>
<td>trans-stilbene</td>
<td>7.76</td>
<td>7.60 (^l)</td>
<td></td>
<td></td>
<td>8.39</td>
<td>7.94</td>
<td>8.37</td>
<td>7.87</td>
</tr>
</tbody>
</table>


Fig. 2.—Plot of measured ionization potentials \((I_{\text{obs}})\) against the calculated ionization potentials \((I_{\text{calc}})\).
except that for perylene where the deviation is 0.25 eV; such a plot might be useful in an empirical sense for the prediction of ionization potentials since the calculations are simple and require only a few seconds of computer time. The equation for the line is:

\[ I = 1.15 I_{\text{cal}}, -1.30 \]  

(1)

Table 2.—OBSERVED AND CALCULATED HIGHER IONIZATION POTENTIALS

<table>
<thead>
<tr>
<th>molecule</th>
<th>PS ( I_a ) values/eV</th>
<th>( n^+ I_a ) values/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>anthracene</td>
<td>8.59, 9.20, 10.21, 11.98, 12.58</td>
<td>8.93, 9.48, 10.45, 10.55, 11.87, 12.80</td>
</tr>
<tr>
<td>pyrene</td>
<td>8.30, 9.44, 10.07, 10.70, 11.88, (15.14)</td>
<td>8.71, 9.54, 9.73, 10.32, 11.37, 11.93, 13.00</td>
</tr>
<tr>
<td>perylene</td>
<td>8.50, 10.29, (15.52), (16.75)</td>
<td>9.05, 9.16, 9.29, 9.41, 10.72, 10.94, 11.56, 13.07</td>
</tr>
<tr>
<td>triphenylene</td>
<td>8.59, 9.60, 10.60, 11.98, 13.29, (15.01), (16.66)</td>
<td>9.14, 9.94, 10.19, 11.94, 12.97</td>
</tr>
<tr>
<td>1,2-benzanthracene</td>
<td>7.95, 8.79, 9.29, 9.85, 10.77, (12.44)</td>
<td>8.58, 9.19, 9.63, 10.18, 10.63, 11.36, 12.30, 12.91</td>
</tr>
<tr>
<td>3,4-benzotetraphene</td>
<td>7.89, 8.67, 9.69, 10.48, 11.64, 13.41 (15.07)</td>
<td>8.59, 8.75, 9.41, 9.68, 10.28, 10.63, 10.97, 11.78, 12.53, 12.99</td>
</tr>
<tr>
<td>1,2-benzpyrene</td>
<td>7.85, 8.67, 9.71, 10.46, 11.46, (11.91), (15.21)</td>
<td>8.49, 9.23, 9.32, 10.01, 10.18, 10.86, 11.96, 12.15, 13.10</td>
</tr>
<tr>
<td>( p )-terphenyl</td>
<td>8.83, 10.82, 13.31 (16.87)</td>
<td>9.31, 9.34, 9.38, 9.42, 10.30, 11.77, 12.29, 12.66</td>
</tr>
<tr>
<td>( o )-terphenyl</td>
<td>8.46, (8.85), 10.42, (10.80), (13.41), (14.37), (18.23)</td>
<td>8.91, 9.37, 9.39, 9.93, 10.10, 11.80, 12.19, 12.72</td>
</tr>
<tr>
<td>( m )-terphenyl</td>
<td>8.97, 10.89, 13.43, (16.45), (16.88), (18.04)</td>
<td>8.80, 9.38, 9.89, 10.21, 11.78, 12.26, 12.68</td>
</tr>
</tbody>
</table>

Table 2 shows the higher ionization potentials deduced from the breaks in our photoelectron spectra, together with the values deduced from our SCF calculations (Mulliken approximation) using Koopmans' Theorem. The correspondence between the two sets of values is surprisingly good, considering the errors inherent in the use of Koopmans' Theorem and the fact that our ionization potentials should be adiabatic values, not vertical ones. It seems clear from this comparison that some of our measured potentials refer in fact to unresolved superpositions of different \( \pi \) ionizations.

This work was supported by the Air Force Office of Scientific Research, by the Robert A. Welch Foundation and by the National Science Foundation.