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PHOTOELECTRON SPECTROSCOPIC STUDIES OF SOME ALKOXY PHENALENONES

F. Carnovale, T. H. Gan and J. B. Peel
Department of Physical Chemistry, and Research Centre for Electron Spectroscopy, La Trobe University, Bundoora, Victoria 3083, Australia

and

K.-D. Franz
Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T., 2600, Australia

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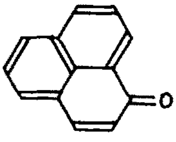
Abstract—The HeI (21.22 eV) vapor phase photoelectron spectra of 1-phenalenone and its 9-substituted OH, OMe, OEt and O n-Bu derivatives have been measured. The low ionization potential regions show characteristic bands arising from π_{cc} and n_o orbitals and their interactions. The assignments are based on data from SPINDO calculations as well as correlations based on a composite-molecule approach. An apparent variation in intramolecular H-bonding in the OH and OMe compounds is explained in terms of Me steric interactions.

Photoelectron (PE) spectroscopy, particularly using the HeI (21.22 eV) ionization source, is now well-established as a technique for structural studies of organic molecules in the gas phase. The use of elevated temperature sample inlet systems allows the study of high molecular weight compounds in the vapor state. Substituted aromatic systems have been widely studied, and the PE spectra of substituted benzenes[1,2] and naphthalenes[3,4] indicate the nature of the data normally investigated for aromatic systems.

For large molecules PE spectroscopic studies generally concentrate on those ionization bands associated with specific electronic features of the structure. These include the π and n orbitals which are mostly found in the low ionization potential (IP) region. Analysis of IP shifts in bands of related molecules leads to quantitative data describing the inductive and resonance effects operating in such systems.[5] In particular cases, the degree of conjugation, both homoconjugative and hyperconjugative, can be estimated.[6]

Recent studies of relevance to organic chemistry includes investigations of conformational equilibria[7,8] and intramolecular hydrogen-bonding.[9,10] The present work on some substituted phenalenones combines many of the above aspects.

The phenalenone nucleus has been isolated as a naturally occurring plant pigment, haemocorin, which is formed in about seventeen species of native Australian plants.[11] Several fungal pigments based on the phenalenone unit have been extracted from the genus *Penicillium*.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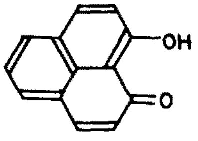
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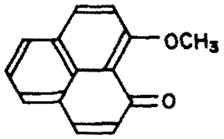
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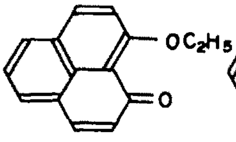
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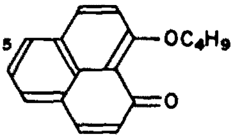
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1-Phenalenone (1) is expected to reveal low IP bands arising from the uppermost of the occupied π molecular orbitals (MOs) and the non-bonding n_o orbital of the carbonyl O atom. The alkoxy derivatives included in the present study are 9-hydroxy-1-phenalenone(2), 9-methoxy-1-phenalenone (3), 9-ethoxy-1-phenalenone(4) and 9-n-butoxy-1-phenalenone(5). Each of these should show a further n_o band arising from the alkoxy group. The overall band distribution in the low IP region will be influenced by various factors including n_o-n_o and π-n_o interactions as well as alkyl inductive effects and the possibility of intramolecular H-bonding.

EXPERIMENTAL

The 9-alkoxy-1-phenalenones (2–5) were prepared in high yields by a modified Ag_2O/alkyl-I method.[12] Their purity was confirmed by mass spectrometric analysis.

The PE spectra were measured on an instrument which has been described.[13] Single scan spectra measured in the analyser sweep mode were obtained for the 7–21 eV IP range in runs typically of 10 min duration. Using a simple resistively heated sample reservoir and target chamber, suitable vapor pressures of each compound were obtained at the following temperatures: (1) 65°, (2) 105°, (3) 175°, (4) 110° and (5) 120°. Calibration of the spectra was achieved using a N_2/acetylene mixture with each sample, for which the operational resolution was ~35 meV. The spectra are shown in Figs. 1 and 2.

The general features of each spectrum are the well-defined low IP bands in the 8–11 eV range with overlapping hydrocarbon bands dominating the 12–19 eV range. It is convenient to confine analysis of the spectra to the low IP range.

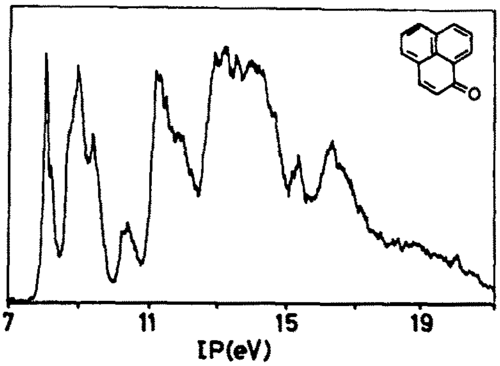

Fig. 1. HeI photoelectron spectrum of 1-phenalenone(1).

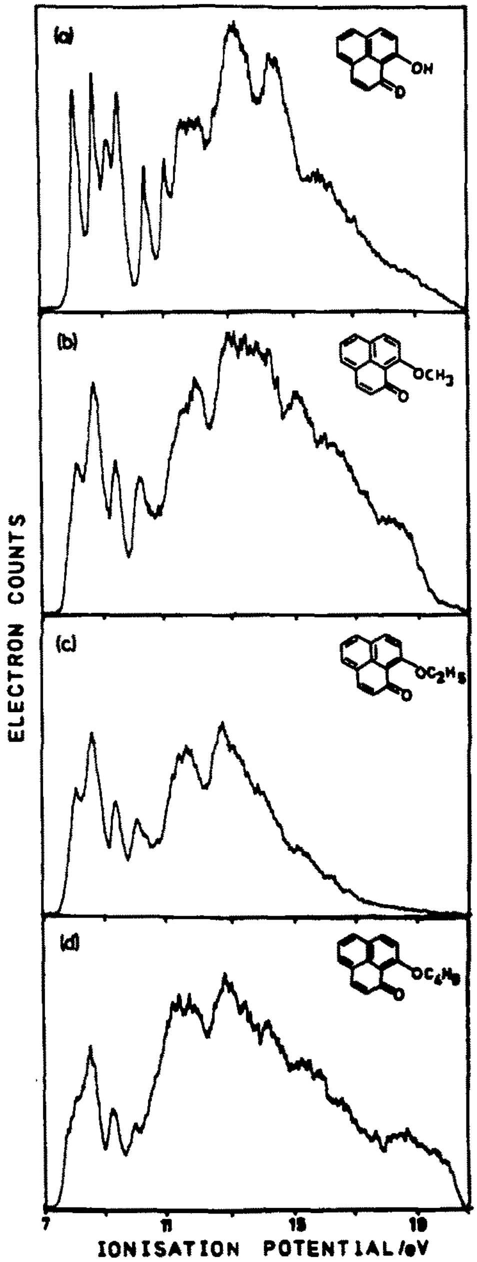

Fig. 2. HeI photoelectron spectra of (a) 9-hydroxy-1-phenalenone(2), (b) 9-methoxy-1-phenalenone (3), (c) 9-ethoxy-1-phenalenone (4), and (d) 9-n-butoxy-1-phenalenone (5).

Calculations. Based on the validity of the Koopmans approximation, numerous semi-empirical and *ab initio* MO methods have been used to derive assignments for PE spectra.

The alkoxy-phenalenones are of such a size that only semi-empirical calculations can be performed with convenience. Accordingly we have used the SPINDO parametrization[14] of the MINDO method,[15] incorporating the H, C and O parameters used in earlier studies on the higher alcohols.[16] These calculations were directed to obtain correlation between eigenvalues and IPs in the low IP range. Conformational variations were investigated in order to evaluate the influence of intramolecular H-bonding.

The molecular geometry used for 1 was based on crystallographic data for pyrene and phenanthrene, which gave C–C bondlengths of 1.35–1.47 Å, and a standard C=O bondlength of 1.15 Å. The uppermost eigenvalues of 1 are listed in Table 1 together with the calculated MO compositions.

For the calculations on 2–5 the phenalenone nucleus was maintained at fixed geometry. Standard bondlengths were used for O–H (0.96 Å), C(ring)–O (1.36 Å), O–C(alkyl) (1.43 Å) and C–C (1.54 Å) and the alkyl groups retained tetrahedral bondangles. The main conformational variations considered were rotation of the alkyl group about the C(ring)–O bond and variation of the C(ring)–O–C(alkyl) bondangle, in particular for the partially closed structures involving close approach of the CO and alkyl groups.

In terms of calculated eigenvalues there is no evidence for intramolecular H-bonding effects in 2. For 3, however, the calculated eigenvalues are very sensitive to the location of the Me group with respect to the CO group. Only for a bifurcated O- -H_2C geometry, with an O- -C separation of 1.69 Å, do the calculations mimic the lowering of the third IP from 9.18 eV to 8.72 eV in going from 2 to 3. The calculated eigenvalues for these optimum geometries are listed in Table 2, together with the corresponding data for 4 and 5. In these latter cases, the same bifurcated O- -H_2C geometry is involved, with the remaining alkyl parts in an open configuration with the carbon skeletons coplanar with the phenalenone nucleus.

The SPINDO carbon charges also show a good correlation with ^{13}C NMR chemical shifts measured for 1, 2, 3 and 4.[17] For the ring C atoms the experimental shifts vary between 114 and 185 ppm, and the SPINDO charges between −0.29 and 0.32. Though the SPINDO charges cannot be regarded as reliable in absolute terms, their correlation with the assigned chemical shifts, as shown in Fig 3, is very good. The worst correlation is obtained for the central phenalene ring carbon which in 3 and 4 shows rather extreme SPINDO charges approaching −0.3.

DISCUSSION

The assignment of the PE spectrum in the low IP range for 1-phenalenone (1) can be described in terms of a composite-molecule model. In the absence of ionization data for phenalene we have based the correlation

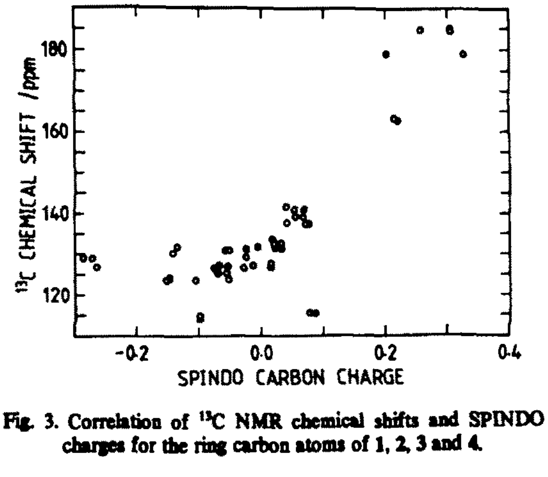

Fig. 3. Correlation of ^{13}C NMR chemical shifts and SPINDO charges for the ring carbon atoms of 1, 2, 3 and 4.

Table 1. Comparison of experimental vertical ionization potentials and calculated eigenvalues for 1-phenalenone (in eV)

IP[a]	MO[b]	ε	Composition %C	%H	%O
8.20	a"	-8.20	97	0	3
8.81	a"	-8.96	100	0	0
9.14	a'	-9.63	52	12	36
9.52	a"	-9.58	100	0	0
10.49	a"	-10.70	95	0	5
11.26	a"	-11.39	100	0	0

a. Accuracy is ∿ ± 0.04 eV

b. Assignment based on composite molecule model in figure 4, and for C_s symmetry.

Table 2. Comparison of experimental vertical ionization potentials and calculated eigenvalues for the 9-alkoxy-1-phenalenones (in eV).

	2			3	
IP[a]	MO[b]	ε	IP[a]	MO[b]	ε
8.12	a"	-8.02	8.14	a"	-7.97
8.75	a"	-8.61	8.64	a"	-8.74
9.18	a'	-9.36	8.72	a'	-8.79
9.53	a"	-9.51	9.38	a"	-9.66
10.34	a"	-10.45	10.30	a"	-10.21
11.00	a"	-11.03	10.64	a"	-11.19

	4			5	
IP[a]	MO[b]	ε	IP[a]	MO[b]	ε
8.06	a"	-8.08	8.03	a"	-8.02
8.61	a"	-8.81	8.51	a"	-8.73
8.77	a'	-8.83	8.66	a'	-9.13
9.42	a"	-9.71	9.40	a"	-9.62
10.11	a"	-10.33	10.11	a"	-10.32
10.62	a"	-11.23	10.51	a"	-11.14

a. Accuracy is ∿ ±0.04 eV.

b. Assignment for C_s symmetry.

diagram, illustrated in Fig. 4, on the naphthalene system, together with estimated IPs for cyclohex-1-ene-one. This latter molecule represents the fragment providing the n_0 and π_{cc} entities in the combination with naphthalene. These IPs for n_0 and π_{cc} have been estimated from the trends observed in related molecules.[18] Clearly the perturbatiion caused by the additional π_{cc} entity is considerable, but it is noteworthy that the interaction is mainly with the naphthalene π MO of similar energy.

The assignment of the third band as involving ionization of the non-bonding n_0 orbital of the carbonyl group is assisted by the observation that since this orbital is of σ symmetry (lying in the plane of the molecule) it does not interact with the π MOs on either side of it energetically. Consequently the three close IPs I_2, I_3 and I_4 can be assigned with adjacent π ionizations well separated as I_2 and I_4.

As indicated in Fig. 1, the band shapes of the first four bands are consistent with this result in that the n_0 ionization is expected to show a broader band than the π ionizations. The SPINDO eigenvalues disagree with this ordering of I_3 and I_4 but the closeness of the calculated eigenvalues indicates that the method overestimates the IP of the n_0 electrons.

Of particular interest in the PE spectra for 2 and 3 are the possible intramolecular H-bonding effects which may be discerned from the experimental IPs. Brown[10] has suggested that a CO n_0 orbital involved in H-bond

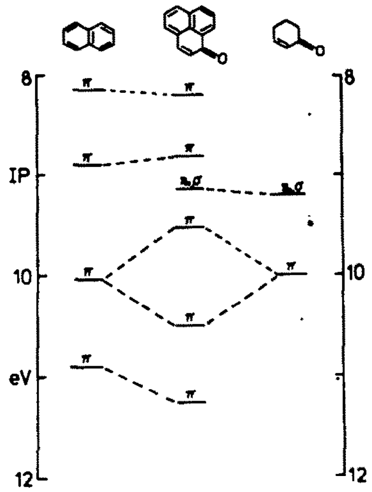

Fig. 4. Composite molecule assignment of the photoelectron spectrum of 1-phenalenone(1).

formation appears at higher IP than its counterpart in a geometric isomer in which H-bonding is precluded. In the case of 2-hydroxycyclohexonone and 2-methoxycyclohexanone the first IPs are 9.70 eV and 9.06 eV respectively, the difference of 0.64 eV being ascribed to intramolecular H-bonding in the former. However the second IPs in each case, assigned to the n_0s of OH and OCH_3, are nearly identical, which is inconsistent with a general comparison of first IPs in related alcohols and ethers.

For 2, there are only small differences in the low IP region of the PE spectrum when compared with 1. Clearly the OH substitution has only a slight effect in marginally lowering the first two IPs. This could involve a balance between inductive and resonance interactions. However the third IP is marginally increased, and this could be attributed to a small H-bonding effect. Alternatively since n_0 on CO is of σ symmetry this shift may be due to a small inductive effect which is not balanced by the resonance interactions occurring in the π system.

The SPINDO eigenvalues show rather larger differences between the two molecules but the shifts in calculated IPs are fairly uniform despite the fact that the geometry used for 2 is most favourable for H-bonding. A composite-molecule correlation between the low IPs of 1 and 2 is shown in Fig. 5. Here the n_0 IP for OH is based on the methanol value of 10.8 eV. In the planar geometry, this n_0 is of π symmetry and interacts with the π MOs of 1, and, according to the SPINDO calculations, with considerable mixing in the MOs corresponding to the fifth and sixth IPs. Hence the assignment for the 10–12 eV region is conveniently summarized as $\pi < n_0(\pi) < \pi$.

For 3, the PE spectrum in the low IP region shows considerable variation to that of 2. There is considerable overlap of the second and third bands, and whereas the first, second, fourth and fifth IPs show only slight reductions from those of 2, the third IP is lowered by 0.46 eV. The composite-molecule correlation diagram for 3 is based on the dimethylether first IP for n_0 in OMe, and as illustrated in Fig. 5 indicates the unusual lowering in the CO n_0 IP. Also the fifth IP is associated with the n_0 of OMe, whereas the SPINDO calculation suggests that it contributes to both the fifth and sixth bands.

The apparently anomalous position of the third IP in this scheme seems to be due to steric effects arising from interaction of the CO and MeO groups and dependent on the closeness of approach of Me to =O. The SPINDO calculations reproduces this lowering of the third IP for a bifurcated $=O--H_2C$ geometry in which the COC bond angle is 126° and the O--C separation is 1.69 Å. Under these conditions the σ_{Me} MO lying in the molecular plane interacts with the CO n_0 of the same symmetry.

In contrast to Brown's description of the differences in n_0 IPs for the 2-hydroxy- and 2-methoxy-cyclohexanones,[10] this explanation regards the OMe substituent as giving rise to the anomalous effect. Since the π IPs corresponding to I_1, I_2 and I_4 are only lowered slightly from their values in 1, then the OMe substitution has only a small overall balance of inductive and resonance effects on the ring orbitals. The considerably greater effect on the CO n_0 of σ symmetry might be considered to be due to a strong through-bond inductive effect in the absence of a balancing resonance effect. However we favor a through-space mechanism arising from σ_{Me} interaction with n_0.

The spectra of 4 and 5 show small IP lowerings in the 8–11 eV region when compared with 3. The first three IPs are similarly assigned to $\pi < \pi < n_0(\sigma)$ and the next three IPs to $\pi < n_0(\pi) < \pi$. The SPINDO calculations agree with this assignment except for the sixth IP in

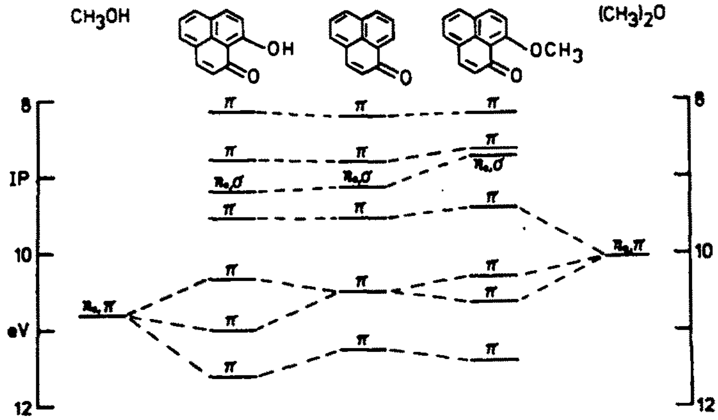

Fig. 5. Composite molecule assignments of the photoelectron spectra of 9-hydroxy-1-phenalenone(2) and 9-methoxy-1-phenalenone(3).

which σ_{cc} character becomes important. Again, close approach of $-CH_2-$ to $=O$ is required in order to describe the third band as $n_O(\sigma)$ character.

CONCLUSION

From their PE spectra the lower IPs of the 9-alkoxy-1-phenalenones have been assigned as $\pi < \pi < n_O(\sigma) < \pi < n_O(\pi) < \pi$. The variations observed in the third IP on OH or OMe substitution of 1-phenalenone are interpreted as indicating a possible marginal intramolecular H-bonding effect in the OH compound, but a considerable effect due to steric interaction in the OCH_3 compound.

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