The Photoelectron Spectra of Some 1,9-Disubstituted Phenalenes

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

The He^{I} vapour phase photoelectron spectra of six 1,9-disubstituted phenalenes have been measured. Data are given for 9-methylaminophenalen-1-one, 9-dimethylaminophenalen-1-one, 9-mercaptophenalen-1-one, 9-methylamino-1-methyliminophenalene, 9-methylaminophenalene-1-thione, and 9-isopropylaminophenalene-1-thione. Observed band shifts in the low ionization energy region (<11 eV) are discussed in terms of substituent lone-pair interactions with the phenalene σ–π molecular network in a manner consistent with the results of SPINDO calculations and a simple correlation procedure. For all compounds the semi-empirical calculations indicate that four of the six uppermost orbitals are ring π orbitals and that two are substituent lone-pair orbitals, one of which is considerably delocalized in nature.

A VARIETY of methods may be employed to interpret the He^{I} photoelectron (p.e.) spectra of large organic molecules. These include both *ab initio* and semi-empirical molecular orbital (MO) calculations, the composite molecule approach,[1] and correlation procedures.[2] We have recently undertaken a p.e. spectroscopic study of a series of 9-alkoxyphenalen-1-one utilizing SPINDO-MO calculations and a simple composite molecule model to arrive at conclusions regarding the nature of p.e. bands in the low energy region in conjunction with an apparent variation in intramolecular hydrogen bonding.[3] The present investigation reports further spectral data on a related series of molecules which are interpreted on the basis of SPINDO-MO calculations with reference to ionization energy (IE) correlation procedures.

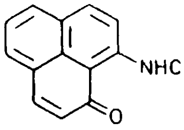
P.e. spectroscopy has become a well established technique in probing both the electronic and structural properties of molecular systems. The conformational behaviour of substituent groups is of particular importance in characterizing a p.e. spectrum.[4] It is therefore of interest to elucidate this aspect in discussing the electronic interactions between a perturbing group and the bulk of a molecule.

The phenalenone nucleus has been isolated as a naturally occurring plant pigment, haemocorin, which is formed in *ca.* 17 species of native Australian plants.[5] Several fungal pigments based on the phenalenone unit have been extracted from the genus *Penicillium*.

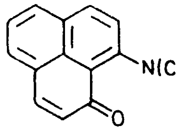
The six substituted phenalenes (1)—(6) included in this study are each expected to reveal six bands in the low IE region arising from the four uppermost ring π molecular orbitals, the nitrogen (or sulphur) lone pair n_N (or n_S) and the corresponding oxygen, sulphur, or nitrogen $n\sigma$ type orbital. However, the overall band distribution may be complicated by n–n and π–n interactions in addition to inductive and steric factors.

EXPERIMENTAL

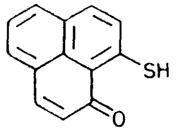
A modified Ag_2O–alkyl–I method was used in the preparation of (1)—(6).[6] The p.e. spectra were measured on an instrument which has been described elsewhere.[7] Single-scan spectra measured in the analyser sweep mode were obtained for the 6—21 eV IE range in runs typically of 10-min duration. Using a simple resistively heated sample reservoir and target chamber, suitable vapour pressures of each compound were obtained at the following temperatures: (1), 140; (2), 90; (3), 110; (4), 85; (5), 120; and (6), 125 °C. Sample purity was ascertained by mass-spectral analysis prior to the running of each sample. Calibration of the spectra was achieved using a nitrogen–acetylene–butadiene mixture with each sample, for which the operational resolution was *ca.* 60 meV. The spectra are shown in Figures 1 and 2.



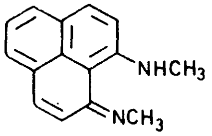
(1)



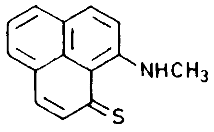
(2)



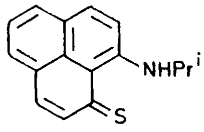
(3)



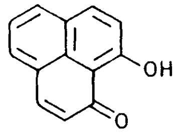
(4)



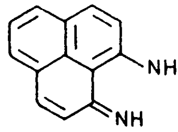
(5)



(6)



(7)



(8)

Analysis of the spectra is confined to the low IE region due to profuse overlapping of bands above 11 eV. The spectrum of (1) is composed of six well resolved bands below 11 eV but those of (2)—(6) are less well resolved. This variation in band resolution arises partly due to band overlap, although the possibility of conformational mixing should also be considered. The lowest six vertical IEs of (1)—(6) are listed in the Table, where they are compared with the calculated IEs and orbital compositions.

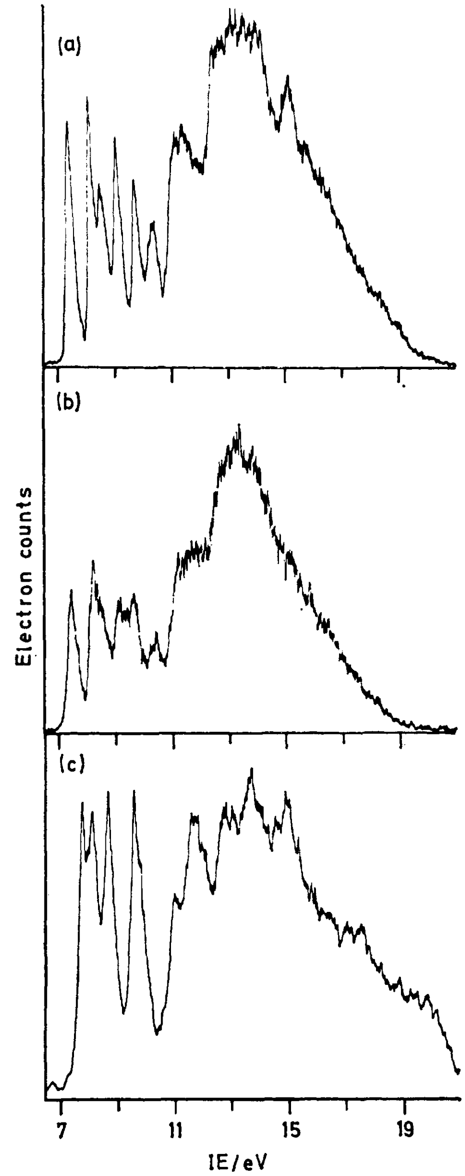


FIGURE 1 He^{I} Photoelectron spectra of (a) 9-methylamino-phenalen-1-one (1), (b) 9-dimethylaminophenalen-1-one (2), and (c) 9-mercaptophenalen-1-one (3)

CALCULATIONS

The advantages of utilizing theoretical SCF-MO calculations, be they *ab initio* or semi-empirical, in interpreting p.e. spectra are so widely acknowledged that few current assignments in the literature are made without employing some form of such calculation. However, the practical necessity for a relatively fast, economical MO method forces the use of semi-empirical calculations for the analysis of large organic molecules such as the substituted phenalenes.

The semi-empirical CNDO- and INDO-MO methods [8] have in the past been used to calculate various physical properties for very large systems. However, the use of the Koopmans' approximation to interpret photoelectron spectra often requires a linear regression analysis.[9] Otherwise, the deviation of calculated IEs from experimental ones are normally *ca.* 2 eV.

The semi-empirical SPINDO method as developed by Lindholm and his co-workers [10] is capable of yielding better correlation between photoelectron data and calculated IEs. The molecular geometry chosen for the phenalene unit was based on crystallographic data for pyrene and phenanthrene, which gave C–C bond lengths of 1.35—1.47 Å. All substituent bond lengths and angles were given standard values.

In the case of the alkylamino-groups in particular, conformational variations have a considerable influence on the interaction of the substituent n_N electrons with the ring π electrons. This is shown by the SPINDO results, though the calculated IEs ($-\varepsilon$) shown in the Table are for conformations where both the alkyl group and hydrogen atom lie out of, and on the same side of, the plane of the phenalene ring, thus allowing maximum n_N–π interaction. The exception is the dimethylamino-group where non-bonded interaction with the carbonyl group occurs for this conformation. The SPINDO results for (2) are consequently for the conformation obtained when the dimethylamino-group is then rotated by 30° about the N–C(ring) bond.

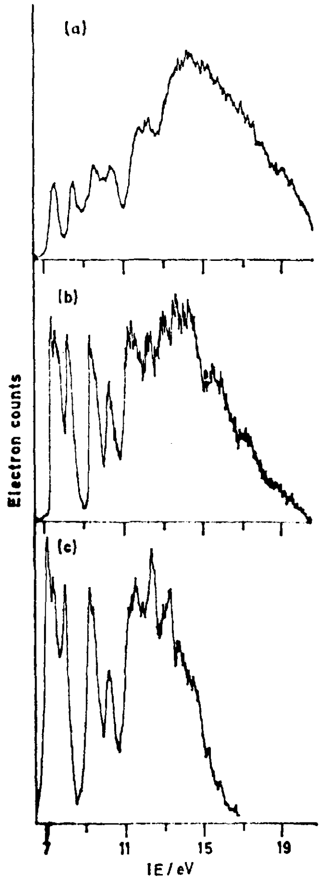


FIGURE 2 He^{I} Photoelectron spectra of (a) 9-methylamino-1-methyliminophenalene (4), (b) 9-methylaminophenalene-1-thione (5), and (c) 9-isopropylaminophenalene-1-thione (6)

For the mercapto-group in (3), the losed hydrogen-bonded geometry gives marginally better theoretical IEs than the planar open geometry, so the former are given in the Table. For the methylimino-group in (4), the preferred conformation is with the CH_3 group aligned with the phenalene plane but directed away from the methylamino-substituent.

The calculated SPINDO carbon charges show a reasonable correlation with the ^{13}C n.m.r. chemical shifts obtained for (1)—(6).[11] For the ring carbon atoms the experimental shifts vary between 107 and 196 p.p.m., and the SPINDO charges between -0.18 and 0.31. As shown in Figure 3, the charge-shift correlation is good except for C-9 and -9b.

Comparison of experimental and calculated ionization energies (in eV) and molecular orbital compositions of the substituted phenalenes (1)—(6)

(1)			(2)			(3)		
IE [a]	$-\varepsilon$ [b]	MO [c]	IE [a]	$-\varepsilon$ [b]	MO [c]	IE [a]	$-\varepsilon$ [b]	MO [c]
7.41	7.97	π–n_N	7.36	8.23	π	7.76	7.87	π-n_S
8.16	8.49	π–n_N	8.14	8.78	π–n_N	8.17	8.41	π–n_S
8.56	9.49	π	8.36	9.62	π–n_N	8.61	9.19	$n_O\sigma$
9.12	9.64	$n_O\sigma$	9.14	9.67	$n_O\sigma$	9.40	9.35	π
9.72	9.98	π–n_N	9.57	10.03	π–n_N	9.71	9.86	n_S–π
10.41	10.83	π	10.32	10.73	π	10.81	10.67	π

(4)			(5)			(6)		
IE [a]	$-\varepsilon$ [b]	MO [c]	IE [a]	$-\varepsilon$ [b]	MO [c]	IE [a]	$-\varepsilon$ [b]	MO [c]
6.98	7.34	π–n_N	7.21	7.82	$n_S\sigma$–n_N	7.17	7.91	$n_S\sigma$–n_N
7.88	8.05	π–n_N	7.40	8.09	π–π_{CS}	7.41	8.12	π–π_{CS}
8.65	8.98	π	8.04	8.79	π–$n_S\sigma$	7.91	8.78	π–$n_S\sigma$
8.94	9.53	π–$n_N\sigma$	9.18	9.44	π	9.02	9.49	π
9.29	9.77	π–$n_N\sigma$	9.30	10.05	π–π_{CS}	9.26	10.10	π–π_{CS}
9.81	10.14	π–n_N	9.96	10.31	π–π_{CS}	9.80	10.31	π–π_{CS}

[a] Accuracy is ± 0.04 eV. [b] By SPINDO calculation. [c] Contributions to the calculated MOs include π (representing phenalene carbon π), π_{CS} (the thione group), n_N and n_S (group orbitals of π symmetry), $n_O\sigma$, $n_N\sigma$, and $n_S\sigma$ (group orbitals of σ symmetry).

DISCUSSION

The SPINDO calculations indicate that for each of the substituents considered there is strong π–π interaction with the phenalene ring π system. However where the substituent at the 1-position has a localized, generally non-bonding, orbital of σ symmetry, it tends to remain of reasonably local character. This is the case for phenalenone and the alkoxyphenalenones[3] where the third IE was assigned as $n_O\sigma$. It is likely that $n_S\sigma$ in the phenalenthiones (5) and (6) and $n_N\sigma$ in the phenalenimine (4) behave similarly.

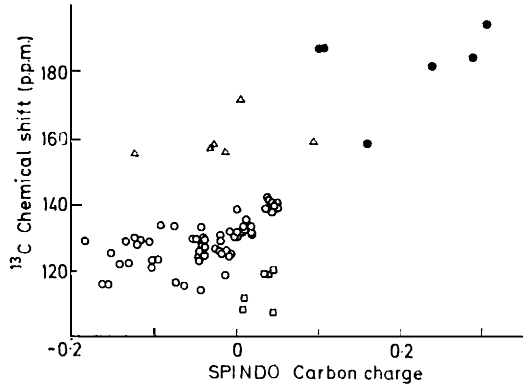


FIGURE 3 Correlation of ^{13}C n.m.r. chemical shifts and SPINDO charges for the ring carbon atoms of (1)—(6): C-1 ●; C-9 △; C-9b □

However, for the six molecules included in the present study, except for (3), the geometry of the 9-substituent is such that the C_s symmetry conferred by the phenalene ring is lost. This results in a certain degree of σ–π mixing occurring in the SPINDO MOs. This is probably exaggerated, in that it is likely that the $n_S\sigma$ and $n_N\sigma$ orbitals do retain a localized identity despite this perturbation.

Consequently an IE correlation procedure, in which the p.e. data for (1)—(6) are compared with those for 9-hydroxyphenalen-1-one (7)[3] and 9-aminophenalen-1-imine (8)[12] has been used to suggest a more convincing assignment of the low IE region of the six molecules. The correlation diagram shown in Figure 4 involves ordering (1)—(6) according to decreasing value of their first IE, with (7) and (8) placed at each end. This order is convenient because it has the phenalenones being followed by the phenalenethiones with the phenalenimines completing the sequence.

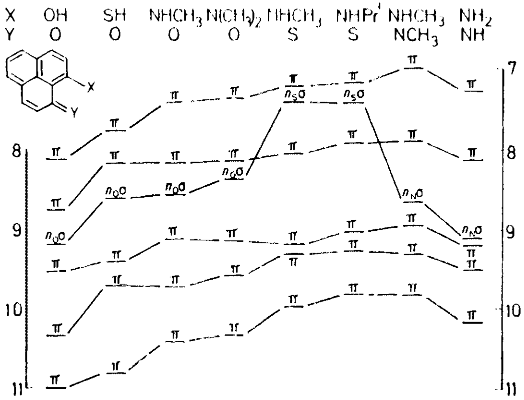


FIGURE 4 Ionization-energy correlation diagram comparing (1)—(6) with the related molecules 9-hydroxyphenalen-1-one (7) and 9-aminophenalen-1-imine (8)

The correlation diagram shows that the remaining four IEs of π symmetry, below 11 eV, also generally decrease through the series. This can be regarded as paralleling the trends in electronegativity of the substituent pairs.

Among the phenalenones, the gradual decrease in the third IE for (3), (1), and (2) is in contrast to the higher third IE of (7). The replacement of OH by SH would be expected to have, due to the strong π_{S} mixing with the phenalene π orbitals, a consistent effect on the π IEs, which is the case, but a lesser effect on the $n_{O}\sigma$ IE. That this does not happen is an indication that a stronger intramolecular hydrogen bond exists in (7) than in (3) or (1), and which stabilizes the $n_{O}\sigma$ orbital as suggested by Brown *et al.*[13] This result differs from our earlier conclusion regarding intramolecular hydrogen bonding in the alkoxyphenalenones.[3]

The phenalenethiones (5) and (6) have their second IEs assigned as the $n_{S}\sigma$ orbital. In a comparison of (1) and (5) where =O has been replaced by =S, the first two π IEs are reduced by a mean of only 0.16 eV whereas the $n\sigma$ IE changes by 1.16 eV. This is consistent with the difference of 1.26 eV between the first IEs of acetaldehyde (10.24 eV)[14] and thioacetaldehyde (8.98 eV)[15] which are assigned to $n_{O}\sigma$ and $n_{S}\sigma$ orbitals respectively.

By comparison the first IE of ethylideneamine,[16] which is assigned to $n_{N}\sigma$, is 10.18 eV, whereas that of *trans*-ethylidene-*N*-methylamine[17] is 9.50 eV. Consequently the difference of 0.46 eV in the third IEs of (4) and (8), assigned as $n_{N}\sigma$, is consistent with this data, and the comparison of the $n_{O}\sigma$ IE of (1) (8.56 eV) and the $n_{O}\sigma$ IE of (4) (8.65 eV) reflects the proximity of the corresponding IEs in acetaldehyde (10.24 eV) and ethylideneamine (9.90 eV).[16] While oxygen and nitrogen differ in electronegativity, the similarity of the IEs of comparable $n_{O}\sigma$ and $n_{N}\sigma$ orbitals is due to the slightly bonding nature of the $n_{N}\sigma$ orbital affecting an increase in its IE.

A further feature of the correlation diagram is that where two IEs are reasonably close they are generally of different symmetry. Consequently the $n\sigma$ band in each of these molecules tends to overlap an adjacent π band. Alternatively, except for the fourth and fifth bands of (5) and (6), the π bands tend to be reasonably spaced. In the cases of (5) and (6), the SPINDO calculations indicate that π_{CS} character is involved in the low IEs, whereas in the phenalenones and phenalenimines the respective π_{CO} and π_{CN} orbitals, being higher in IE, contribute mainly to the π states above 11 eV.

Conclusions.—Both the amino- and mercapto-substituents are known to interact strongly with the π orbitals of planar aromatic systems. This is illustrated by the examples of aniline and the *N*-methylanilines,[18] and by thiophenol[19] in which the mercapto-group behaves like the vinyl group in styrene.

For the 1,9-disubstituted phenalenes considered here, the $n_{N}\pi$ orbital of the alkylamino-groups and the $n_{S}\pi$ orbital of the mercapto-group behave similarly, and due to strong interaction with the phenalene ring, are considerably delocalized through the π-orbital system. This is confirmed by semi-empirical SPINDO calculations.

By comparison the localized σ orbitals of the oxo-, thioxo-, and imino-substituents retain their identity to a large degree, their IEs showing similar relationships to the corresponding data for smaller molecules. The 9-substituted phenalen-1-ones and phenalen-1-imines hence have their first six ionizations designated as $\pi < \pi < n\sigma < \pi < \pi < \pi$ whereas the 9-substituted phenalene-1-thiones show the pattern $\pi < n\sigma < \pi < \pi < \pi < \pi$.

We acknowledge the La Trobe Postgraduate awards held by F. C. and T. H. G.

[9/866 *Received, 5th June,* 1979]

REFERENCES

[1] J. W. Rabalais, 'Principles of Ultraviolet Photoelectron Spectroscopy,' Wiley, New York, 1977.

[2] M. Bloch, F. Brogli, E. Heilbronner, T. B. Jones, H. Prinzbach, and O. Schwikert, *Helv. Chim. Acta*, 1978, **61**, 1388 and references therein.

[3] F. Carnovale, T. H. Gan, J. B. Peel, and K.-D. Franz, *Tetrahedron*, 1979, **35**, 129.

[4] J. P. Maier, *Helv. Chim. Acta*, 1974, **57**, 994.

[5] D. H. Reid, *Quart. Rev.*, 1965, **19**, 274.

[6] K.-D. Franz and R. L. Martin, *Tetrahedron*, 1978, **34**, 2147.

[7] R. G. Dromey and J. B. Peel, *Austral. J. Chem.*, 1975, **28**, 2353.

[8] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[9] G. D. Purvis and Y. Ohrn, *J. Chem. Phys.*, 1974, **60**, 4063.

[10] E. Lindholm, C. Fridh, and L. Asbrink, *Faraday Discuss.*, 1972, **54**, 127.

[11] K.-D. Franz, *Org. Chem.*, 1979, **44**, 1704.

[12] F. Carnovale, T. H. Gan, and J. B. Peel, *J. Electron Spectroscopy Related Phenomena*, 1979, **15**, 173.

[13] R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *J. Amer. Chem. Soc.*, 1979, **101**, 3157.

[14] D. Chadwick and A. Katrib, *J. Electron Spectroscopy Related Phenomena*, 1974, **3**, 39.

[15] H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Letters*, 1974, **29**, 265.

[16] D. C. Frost, B. Macdonald, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectroscopy Related Phenomena*, 1978, **14**, 379.

[17] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 684.

[18] D. W. Turner, *Phil. Trans. Roy. Soc.*, 1970, **A268**, 7.

[19] R. A. W. Johnstone, and F. A. Mellon, *J.C.S. Faraday II*, 1973, 1155.