

CCA-1126

YU ISSN 0011-1643

547.672

Original Scientific Paper

Photoelectron Spectroscopy of 9-Substituted Anthracenes

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Received July 7, 1978

The HeI photoelectron (PE) spectra of anthracene and ten of its 9-substituted derivatives with methyl, *tert*-butyl, fluoro, chloro, bromo, methoxy, aldehyde, cyano, nitro and phenyl groups as substituents have been recorded. Systems arising from π -ionizations are assigned. The assignment is supported by molecular orbital calculations. The effect of the substituent on the lowest ionization energy is well described by Hammett substituent constants based on the benzene system.

INTRODUCTION

The question of the electronic structure of 9-substituted anthracenes arose in course of our recent study of their electron impact induced fragmentation¹. It was supposed that the electronic structure might be responsible for the different behaviour regarding the loss of substituent. Photoelectron (PE) spectroscopy is effective in getting information concerning electronic structures of molecules within the concept of occupied molecular orbitals (Koopmans' theorem). Regarding the ionization process it is also a complementary method to low energy mass spectrometry. As opposed to anthracene²⁻⁶ the substituted anthracenes were scarcely studied by PE spectroscopy⁶⁻⁹. Recently, ionization energies determined mass spectrometrically¹⁰ as well as a comparison between ionization energies and charge transfer excitation energies of their TCNE and TCNQ complexes¹¹ have been reported for several *meso*-substituted anthracenes.

EXPERIMENTAL

The PE spectra of anthracene and the ten 9-substituted anthracenes were recorded on a Vacuum Generators UV-G3 instrument using the HeI line for excitation. For details of the instrument, see ref 12. Elevated temperature of the sample inlet system (120—180 °C) was employed to produce satisfactory spectra. The energy scale was calibrated and controlled by admitting an Ar/Xe gas mixture to the sample. Besides anthracene, the PE spectra of all compounds were recorded at low resolution (15 meV and 35 meV, respectively). The accuracy of the ionization energies quoted is better than 0.03 eV. The anthracenes are either of commercial origin (anthracene,

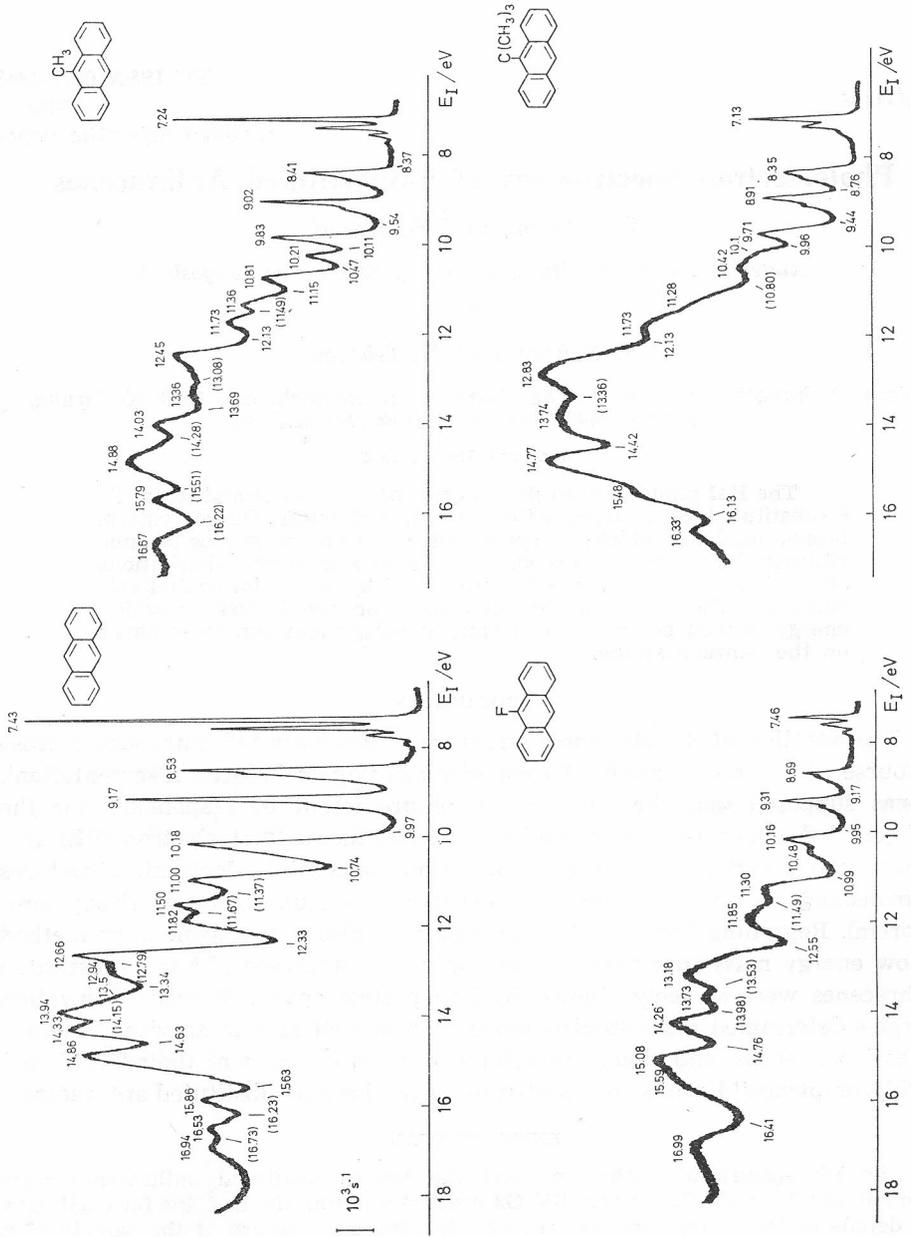


Figure 1. HeI photoelectron spectra of anthracene, 9-methylanthracene, 9-tert-butylanthracene and 9-fluoroanthracene.

9-methyl- and 9-phenylanthracene) or were synthesized by procedures well described in the literature. All compounds were purified by column chromatography on Al_2O_3 in benzene or cyclohexane and final recrystallization.

RESULTS AND DISCUSSION

The PE spectra of anthracene, 9-methylanthracene, 9-*tert*-butylanthracene and 9-fluoroanthracene (Figure 1), 9-chloroanthracene and 9-bromoanthracene (Figure 2) and those of 9-anthraldehyde, 9-methoxyanthracene, 9-cyanoanthracene and 9-nitroanthracene (Figure 3) are reproduced. The characteristic values of the maxima («vertical ionization energies») and onsets («adiabatic ionization energies») of the systems observed are listed above and below the spectra, respectively. Uncertain values are given in parentheses.

High resolution measurements on anthracene showed that the first four systems exhibit a vibrational fine structure with a progression in 1400 cm^{-1} (\tilde{X}), 320 and 750 cm^{-1} (\tilde{A}), 600 and 1400 cm^{-1} (\tilde{B}) and 1100 cm^{-1} (\tilde{C}). The most

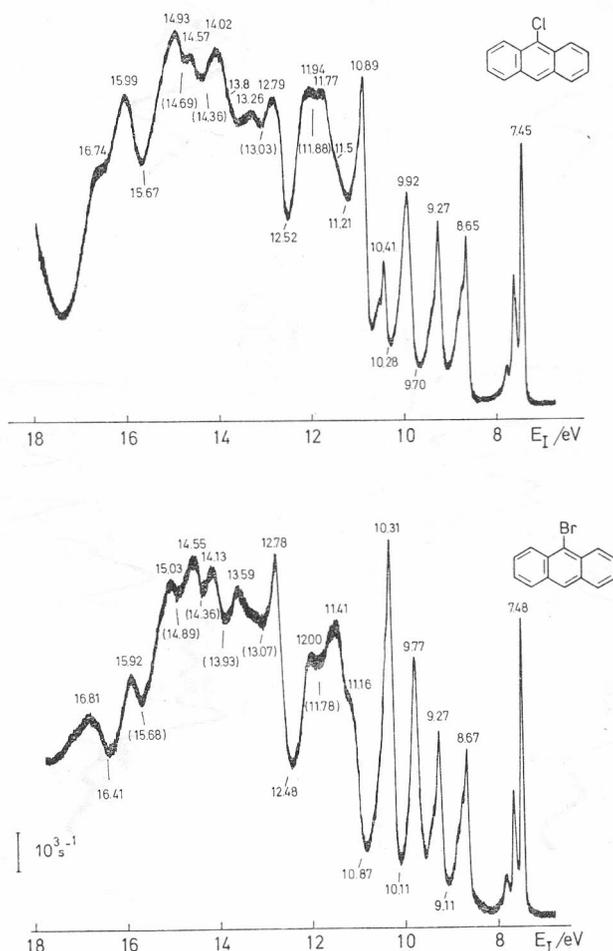


Figure 2. HeI photoelectron spectra of 9-chloroanthracene and 9-bromoanthracene.

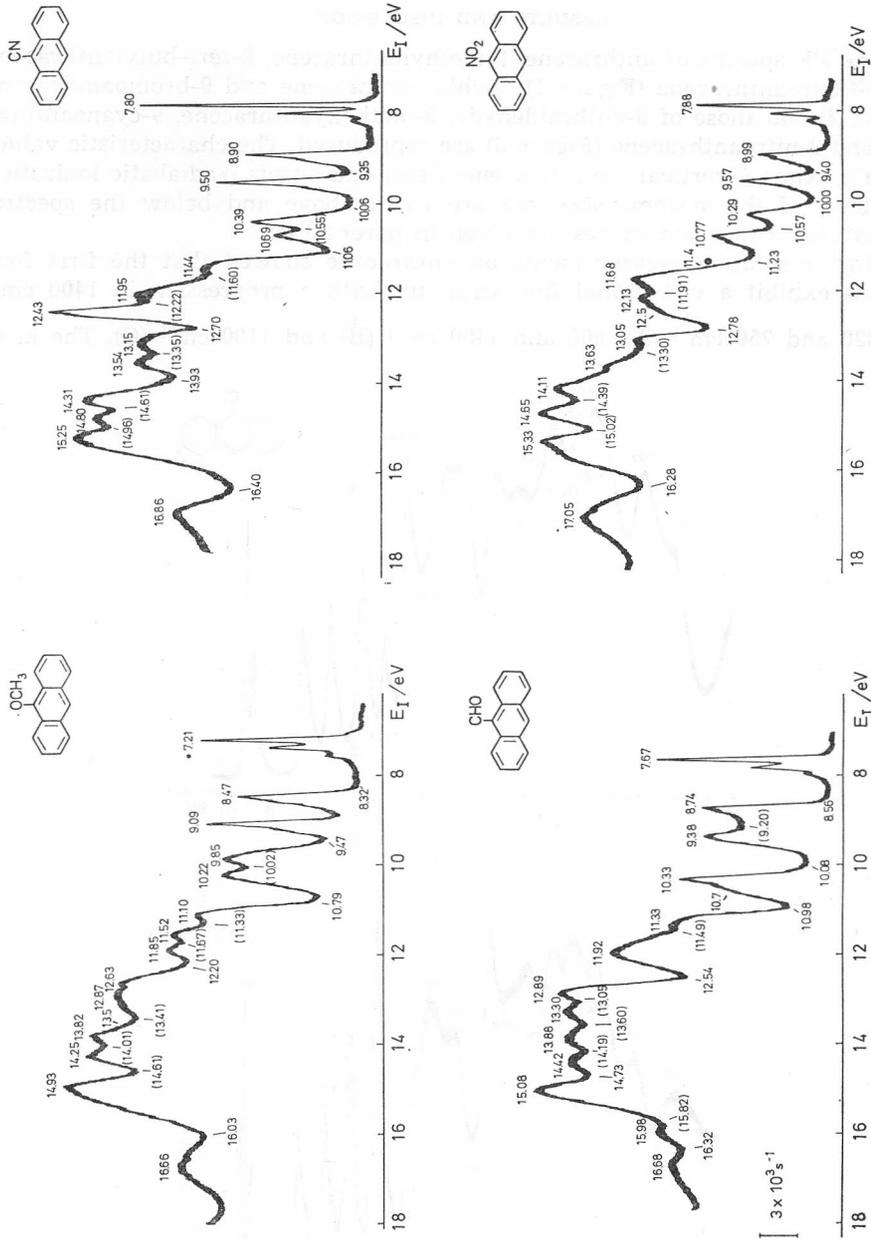


Figure 3. He I photoelectron spectra of 9-methoxyanthracene, 9-anthraldehyde, 9-cyanoanthracene and 9-nitroanthracene.

prominent progression in 1400 cm^{-1} of the \tilde{X} -system is characteristic of all compounds investigated and can readily be observed at low resolution. This progression is also observed in PE and electronic absorption spectra^{4,13} of other polycyclic aromatic hydrocarbons, representing a normal vibration that involves alternate stretching of adjacent CC bonds⁴. For the assignment of individual band systems in the PE spectra, semiempirical SCF MO calculations within the framework of Pariser, Parr and Pople's (PPP) method were performed.

In the PPP calculations standard molecular geometries and parameters were employed (Table I). The resulting canonical SCF MO energies of the π -orbitals for the calculated molecules are given in Table II.

TABLE I
Parameters Used in PPP Calculations

Atom	$W_{\mu+}/\text{eV}$	$\gamma_{\mu\mu+}/\text{eV}$	$\beta_{C-\mu}/\text{eV}$	$r_{C-\mu}/\text{pm}$
C	11.16	11.13	-2.39	140
Cl	24.01	11.27	-0.93	171
Br	21.65	10.03	-0.70	186
CH ₃ O	26.65	14.53	-2.55	136
CHO	α_{O} 11.16 α_{O} 17.7	γ_{C} 11.13 γ_{O} 15.23	-2.65	122
CN	α_{C} 11.16 α_{N} 14.18 α_{C} 11.16	γ_{C} 11.13 γ_{N} 12.52 γ_{C} 11.13	-3.5	115 148 C—N
NO ₂	α_{N} 19.72 α_{O} 17.28	γ_{N} 14.80 γ_{O} 15.27	-2.37	122 N—O

* 1 eV \approx 96.487 kJ mol⁻¹

TABLE II
Canonical SCF MO Energies in the Ground State of 9-Substituted Anthracenes in Electron Volts

9-X-Anthracene	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6	ϵ_7	ϵ_8	ϵ_9	ϵ_{10}	
H	14.38	13.26	11.59	11.59	10.36	10.13	8.54				
Cl	14.47	13.38	13.13	11.75	11.55	10.57	10.33	8.64			
Br	14.46	13.37	12.11	11.74	11.44	10.60	10.32	8.70			
CH ₃ O	14.78	13.33	13.22	11.53	11.02	10.33	10.09	8.22	CH ₃ -inductive		
CHO	14.76	13.41	13.24	11.75	11.51	10.49	10.29	8.76			
CN	14.79	13.45	13.39	11.72	11.45	10.49	10.24	8.66			
NO ₂	20.90	16.83	15.80	14.14	13.96	12.91	12.61	11.02	9.56		
Ph	planar	14.59	13.47	13.25	11.88	11.58	10.36	10.35	10.31	10.12	8.29
	35° rot.	14.51	13.43	13.25	11.80	11.58	10.36	10.35	10.32	10.12	8.36

The assignment of the four lowest energy ionizations known to be of π -type is in agreement with a linear relationship with calculated orbital energies, naturally implying the validity of Koopmans' theorem. Assuming that the linear correlation also holds for the corresponding systems in the π -type allows one to predict the positions of the corresponding systems in the PE spectrum within a range of about 0.5 eV. An inspection of the PE spectra at these positions usually yields an assignment supported also by the characteristic shape of such peaks. Thus, for anthracene (Figure 1, upper left) the systems at 7.43 (π_7), 8.53 (π_6), 9.17 (π_5), 10.18 (π_4 and π_3), 11.82 (π_2) and 13.5 eV (π_1) were assigned as π -ionizations, indicating systems at 11.0, 11.50, 12.66 and 12.94 eV in this region as σ -ionizations. The procedure mentioned above also allowed the prediction of π -ionization energies of those substituted anthracenes which were calculated by the PPP-method. The assignment of the system at 13.5 eV in anthracene as π_1 is also in agreement with the position of that ionization in phenanthrene (at about 14 eV)¹⁴.

However, the assignment of π -ionizations in 9-methyl-, 9-*tert*-butyl- and 9-fluoroanthracene (Figure 1) can easily be deduced by comparison with the PE spectrum of anthracene and by taking into account the inductive effects of the alkyl and fluoro substituents¹⁵. Thus, systems at 7.24 and 7.13 (π_7), 8.41 and 8.35 (π_6), 9.02 and 8.91 (π_5), 9.83 and 9.71 (π_4), 10.21 and 10.1 (π_3) as well as at 11.73 and 11.73 eV (π_2) are easily recognized in the 9-methyl- and 9-*tert*-butylanthracene spectra, respectively. The position of π_1 is less certain, but systems at 13.36 and 13.74 could correspond to the anthracene system at about 13.5 eV, which was assigned as π_1 ionization. Similarly, for 9-fluoroanthracene, systems at 7.46 (π_8), 8.69 (π_7), 9.31 (π_6), 10.16 (π_5), 10.48 (π_4), 11.85 (π_3) and 13.73 eV (π_2) were ascribed to π -ionizations. The position of the highest energy π_1 ionization in the PE spectrum of 9-fluoroanthracene is expected to be above 16 eV¹⁶.

In all three compounds the degeneracy of the π_4 and π_3 ionizations of anthracene is lifted by substitution and we observe two systems, of which the one at lower energy has the greater intensity.

For 9-chloro- and 9-bromoanthracene (Figure 2) calculations nicely predict their splitting and the position of the new π -ionization as well. Additionally, the following assignment results:

7.45 (π_8), 8.65 (π_7), 9.27 (π_6), 9.92 (π_5), 10.41 (π_4), 10.89 (n_{Cl}), 11.5 (π_3), 11.94 (π_2) and 13.8 eV (π_1) for 9-chloroanthracene and 7.48 (π_8), 8.67 (π_7), 9.27 (π_6), 9.77 (π_5), 10.31 (n_{Br}), 10.5? (π_4), 11.16 (π_3), 12.00 (π_2) and 13.59 eV (π_1) for 9-bromoanthracene.

In the latter, the lower intensity component of the split anthracene π_4/π_3 systems is hidden by the n_{Br} system.

In the PE spectra of 9-methoxyanthracene, 9-anthraldehyde, 9-cyanoanthracene, and 9-nitroanthracene (Figure 3) ionizations which we can interpret as lone pair as well as π -ionizations can cause some trouble in assignment. Calculations assigning them as π -electrons will tend to predict their energy too high. Thus, for 9-methoxyanthracene, a comparison with calculation would indicate systems at 7.21 (π_8), 8.47 (π_7), 9.09 (π_6), 9.85 (π_5), 10.22 (π_4), 11.52 (π_3 , mainly on oxygen), 11.85 (π_2) and about 13.5 eV (π_1) as π -ionizations. However, the shape of the systems at 9.85 eV and 10.22 eV (lower intensity

component) and the fact that the compound could be interpreted also as an aryl alkyl ether suggest that the »oxygen lone pair ionization« should be expected within the system at 10.22 eV. In this case the ionization at 11.52 eV is a σ -ionization which is also in agreement with the shape of the anthracene and 9-methylanthracene spectra in this region (compare Figure 3 and Figure 1).

In the PE spectrum of 9-anthraldehyde the assignment of the system at 7.67 (π_8) is clear, but besides the π_7 and π_6 ionizations also the in-plane oxygen lone pair ionization must occur in the region between 8.6 and 9.5 eV. Systems at 10.33 and 10.7 (?) eV were assigned as π_5 and π_4 , respectively. The additional π -ionization arising from the C=O bond in the molecule is expected in agreement with calculation (ϵ_3) at high energy together with π_2 at about 11.9 eV. The system at 13.88 eV we tentatively assign as π_1 -ionization.

The electron withdrawing cyano and nitro substituents enhance strongly the energies of π -ionizations. The additional, nearly degenerate, two π -ionizations of the cyano group are well observed at 12.43 eV in the PE spectrum of 9-cyanoanthracene. Besides the completely uncertain position of π_1 (at 13.54 or 14.2 eV), and assuming that π_2 is at about 12.5 eV, the assignment 7.80 (π_8), 8.9 (π_7), 9.50 (π_6), 10.39 (π_5), 10.69 (π_4), 12.43 (π_3 and the additional π_{CN} ionization) can be taken for granted for 9-cyanoanthracene.

Also reasonable, and supported by calculation, is the assignment 7.88 (π_6), 8.99 (π_8), 9.57 (π_7), 10.29 (π_6), 10.77 (π_5), about 11.4 (π_4) and 12.5 (π_3), 13.63 (π_2) and at about 16 eV (π_1) for 9-nitroanthracene. Additionally, by comparison with PE spectra of nitrobenzene and other nitro aromatics¹⁷, an (in-plane) oxygen lone pair ionization is assigned to be within the system at 10.77 eV (low intensity component).

In the PE spectrum of 9-phenylanthracene similarly to Schäfer et al.⁸ we assign systems at 7.18 (π_{10}), 8.37 (π_6), 8.89 (π_8 and π_7), 9.23 (π_6), 9.94 (π_5), 10.21 (π_4), about 11.8 (π_3 and π_2 ?) and 13.6 (π_1) as π -ionizations. The effect of twisting the phenyl ring is negligible within the calculation, but it is very likely that this compound is non-planar. A steric effect, in addition to the electronic effect, is clearly indicated in Figure 4 where a correlation of the lowest energy

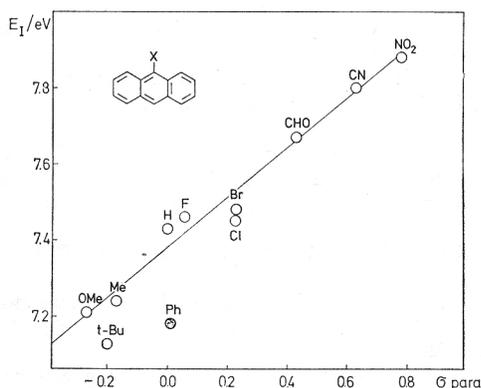


Figure 4. Correlation of the lowest ionization energy of 9-substituted anthracenes with Hammett σ_p constants (from ref 19 and ref 20 (for the aldehyde group)). Full points for *tert* butyl and phenyl are not included in the correlation line.

π -ionization of the 9-substituted anthracenes with Hammett σ_{para} values for benzenes^{19,20} clearly exists for all substituents besides *tert*-butyl and phenyl, which cause sterical hindrance.

The eleven 9-substituted anthracenes in Figure 4 reveal an ionization energy of $E_i = ((0.70 \pm 0.07) \text{ eV}) \sigma_p + ((7.34 \pm 0.03) \text{ eV})$ with a correlation coefficient of $r = 0.956$. Omitting the two sterically hindered 9-phenyl- and 9-*tert*-butylantracenes from Figure 4 results in $E_i = ((0.64 \pm 0.04) \text{ eV}) \sigma_p + ((7.38 \pm 0.02) \text{ eV})$ with a correlation coefficient of $r = 0.984$. Since we are dealing with ground state σ -values obtained from kinetic data on mono-substituted benzenes, the correlation is surprisingly good and appears to be no worse than those for other spectroscopic correlations with Hammett σ -values²¹. Furthermore, the correlation of the lowest energy π -ionization of the 9-substituted anthracenes with Hammett σ -values is of the same quality as the one between the lowest ionization energy of benzenes and σ_{para} values²², indicating that, similar to the *para*-position in benzene, the 9-position in anthracenes is highly sensitive to electronic effects and that the response in both classes of molecules is the same.

Acknowledgment. — This work was performed on the basis of a German-Yugoslav scientific cooperation program. The financial support by the *Internationales Büro, Kernforschungsanlage Jülich*, and by the *Republic Council for Science of Croatia (SIZ II)* is gratefully acknowledged. We thank Dr. J. Michl from the University of Utah, Salt Lake City, for a sample of 9-fluoroanthracene.

REFERENCES

1. H. Güsten, L. Klasinc, S. Komadinović, and D. Stefanović, *Croat. Chem. Acta* **48** (1976) 109.
2. J. H. D. Eland, *Int. J. Mass Spectrom.* **9** (1972) 214.
3. M. J. S. Dewar and D. W. Goodman, *J. Chem. Soc. Faraday Trans. II* **68** (1972) 1784.
4. R. Boschi, J. N. Murrell, and W. Schmidt, *Discuss. Faraday Soc.* **54** (1972) 116.
5. P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta* **55** (1972) 1415.
6. D. G. Streets and T. A. Williams, *J. Electron Spectrosc.* **3** (1974) 71.
7. N. S. Hush, A. S. Cheung, and P. R. Hilton, *J. Electron Spectrosc.* **7** (1975) 385.
8. W. Schäfer, A. Schweig, F. Bickelhaupt, and H. Vermeer, *Angew. Chem.* **84** (1972) 993.
9. S. Hino and H. Inokuchi, *Chem. Lett.* (1974) 363.
10. K.-H. Grupe, M. Ruhtenberg, and K.-H. Heckner, *Z. Chem.* **16** (1976) 20.
11. J. Sauer, J. Bendig, and M. Siegmund, *Z. Chem.* **17** (1977) 308.
12. L. Klasinc, B. Kovač, and B. Ruščić, *Kem. Ind. (Zagreb)* **23** (1974) 569.
13. J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*, Methuen, London, 1963.
14. B. Ruščić, B. Kovač, L. Klasinc, and H. Güsten, *Z. Naturforsch.* **33a** (1978) 1006.
15. H. Güsten, L. Klasinc, and B. Ruščić, *Z. Naturforsch.* **31a** (1976) 1051.
16. W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *Chem. Phys. Lett.* **45** (1977) 295.
17. T. Kobayashi and S. Nagakura, *J. Electron Spectrosc.* **6** (1975) 421.
18. L. Klasinc, B. Ruščić, G. Heinrich, and H. Güsten, *Z. Naturforsch.* **32b** (1977) 1291.
19. H. H. Jaffé, *Chem. Rev.* **53** (1953) 191.

20. A. A. Humffray, J. J. Ryan, J. P. Warren, and Y. H. Yung, *Chem. Commun.* (1965) 610.
21. A. R. Katritzky and R. D. Topsom in: N. B. Chapman and J. Shorter, (Eds.), *Advances in Linear Free Energy Relationships*, Chap. 3, Plenum Press, London and New York, 1972.
22. M. Thompson, P. A. Hewitt, and D. S. Wooliscroft in: D. Briggs, (Ed.), *Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy*, Chap. 10, Heyden, London-Philadelphia-Rheine, 1977.

SAŽETAK

Fotoelektronska spektroskopija 9-supstituiranih antracena

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Snimljeni su HeI fotoelektronski spektri antracena i deset njegovih derivata sa slijedećim supstituentima u položaju 9: metil, *terc.*-butil, fluor, klor, brom, metoksi, aldehyd, cijano, nitro i fenil. Na osnovi molekularno-orbitalnih računa u spektrima su označeni sistemi koji su posljedica ionizacije elektrona. Hammettove konstante za benzenski sistem dobro opisuju efekt supstituenata na najniže energije ionizacije.

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Prispjelo 7. srpnja 1978.