

Ionization Potentials of Some Azoalkanes by Photoelectron Spectroscopy

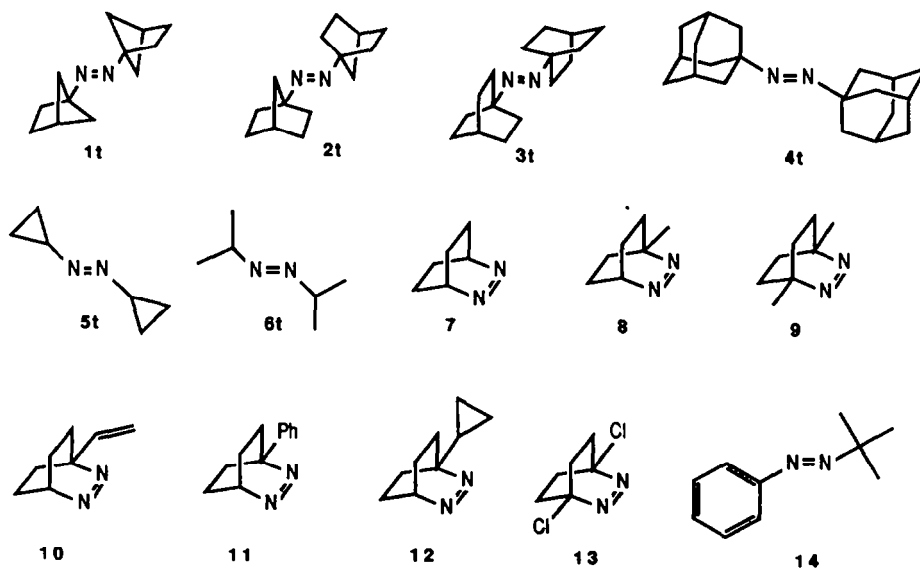
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Abstract Photoelectron spectra have been obtained for a set of azo compounds consisting of three pairs of *cis*, *trans* isomers, seven bridgehead substituted 2,3-diazabicyclo[2.2.2]oct-2-enes (DBO's), and one arylazoalkane. The lowest ionization potentials, which range from 7.83 to 9.21 eV, do not correlate with *cis* ground state energy or photolability of the DBO derivatives. Vibrational fine structure was observed in three DBO's, allowing verification that the lowest ionization takes place from the antibonding combination of nitrogen lone pairs.

Although photoelectron (PE) spectra have been reported for a substantial number of azoalkanes,¹⁻⁶ the availability of several new compounds and the possibility of correlating chemical reactivity with ionization potential (IP) led us to determine the PE spectra of fourteen more azoalkanes. Current interest in chemical^{9,10} and photochemical¹¹⁻¹³ one electron oxidation of azoalkanes to their radical cations¹⁴ and the fact that their electrochemical oxidation is irreversible¹⁵ provided additional motivation for this study. Four of the new data are for *trans* azoalkanes with bridged bi- and tricyclic alkyl groups (1t - 4t) while two more are for the corresponding *cis* isomers (1c, 2c).¹⁶ Counting our results for azocyclopropane (5t, 5c) and azoisopropane (6t, 6c),¹ we have IP's of four *cis*, *trans* pairs.



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The other major set of new compounds are bridgehead substituted 2,3-diazabicyclo[2.2.2]oct-2-enes (DBOs, 7 - 13) whose thermal and photochemical behavior has been studied extensively.^{11, 19-22} Finally, we obtained the first PE spectrum of an alkyl-aryl azo compound 14.²³

As seen in Table I, the lowest IP of cyclic *cis* azoalkanes is always below that of their *trans* isomers, and the IP difference agrees nicely with the 6.9 kcal/mol calculated for diimide.²⁵ It is of interest to attempt a correlation of these IP's with the *cis-trans* energy difference ΔE_{c-t} and with the uv wavelength maximum. The requisite data are shown in Table II.

Table I Ionization Potential (eV) of Azoalkanes^a

Compound	IP (1)	IP (2)	IP (3)
1t	8.44	10.06 ^b	11.30 ^b
1c	7.96	10.18 ^b	11.08 ^b
2t	8.24	10.33	11.47
2c	7.99		
3t	7.86		
4t	7.83		
5t	8.84	9.57	10.84
5c	8.47	10.02	10.60
6t ^c	8.47	11.1 ^b	11.5
6c ^c	8.24	11.18	11.9
7	8.19, 7.95(a)	10.78	
	8.32 ^d , 7.79(a) ^d	10.70 ^d	
8	8.19, 7.84(a)	10.61	
9	8.13, 7.73(a)	10.55	
	8.06 ^c	10.48 ^c	
10	8.34	9.90	10.77
11	8.09	8.90	9.20
12	8.32	10.00	10.58
13	9.21	11.04	11.27
14	8.28	8.95	9.40

a. values listed are vertical IP's unless designated as adiabatic (band onset) by (a). b. not well resolved. c. ref. 1. d. ref. 4a.

Table II Data for *Cis-Trans* Azoalkane Isomers^a

Compound	λ_{\max} , nm	$\Delta\lambda^b$	ΔE_{c-t}^c	ΔIP_{c-t}^d
1t	371			
1c	404	6.3	12.7	11.1
2t	365			
2c	423	10.7	16.1	5.8
5t	335			
5c	345	2.5	4.3	8.5
6t	359			
6c	382	4.8	7.0	5.3

a. most of the data are from refs. 17, 18 and 24. b. difference between λ_{\max} for *cis* and *trans* (kcal/mol). c. thermodynamic *cis-trans* energy difference (kcal/mol). d. IP difference between *cis* and *trans* (kcal/mol).

Viewed simply, greater steric bulk of the R groups should raise the ground state energy and force the nitrogen lone pairs into closer proximity. Since the HOMO of *cis* azoalkanes is the antibonding combination of n orbitals, a higher energy ground state could lower the n -IP and move the uv absorption to longer wavelength.²⁶ Indeed a linear relationship between ground state energy and uv λ_{\max} has been reported previously^{17,18} and is apparent in Table II. On the other hand, ΔIP is unrelated to either $\Delta\lambda$ or $\Delta E_{C-\tau}$; that is, a higher *cis* ground state energy does not produce a corresponding decrease in IP. This attempted correlation employs vertical IP's, which correspond to a constant geometry during ionization. Since the ground state has smaller C=N angles than the radical cation,^{25,26} bulky groups will open these angles more in the ground state, making the vertical IP a function of both *cis* azoalkane geometry and energy.

Seven derivatives of DBO are included in Table I. Introducing bridgehead methyl groups causes a monotonic decrease in IP, seen most readily in the adiabatic values for 7, 8 and 9. However, this decrease is less than half of that found in acyclic azoalkanes.¹ The new IP(1)'s for 7 and 9 differ slightly from those published previously^{1,4} because the present spectra (cf. Fig 1) exhibit vibrational fine structure. We have assigned the IP_v as the mean of the equal intensity vibrational bands of 8 and 9. In the case of 7 where the vibrational progression is most distinct, the IP_v was taken as the position of the strongest band.

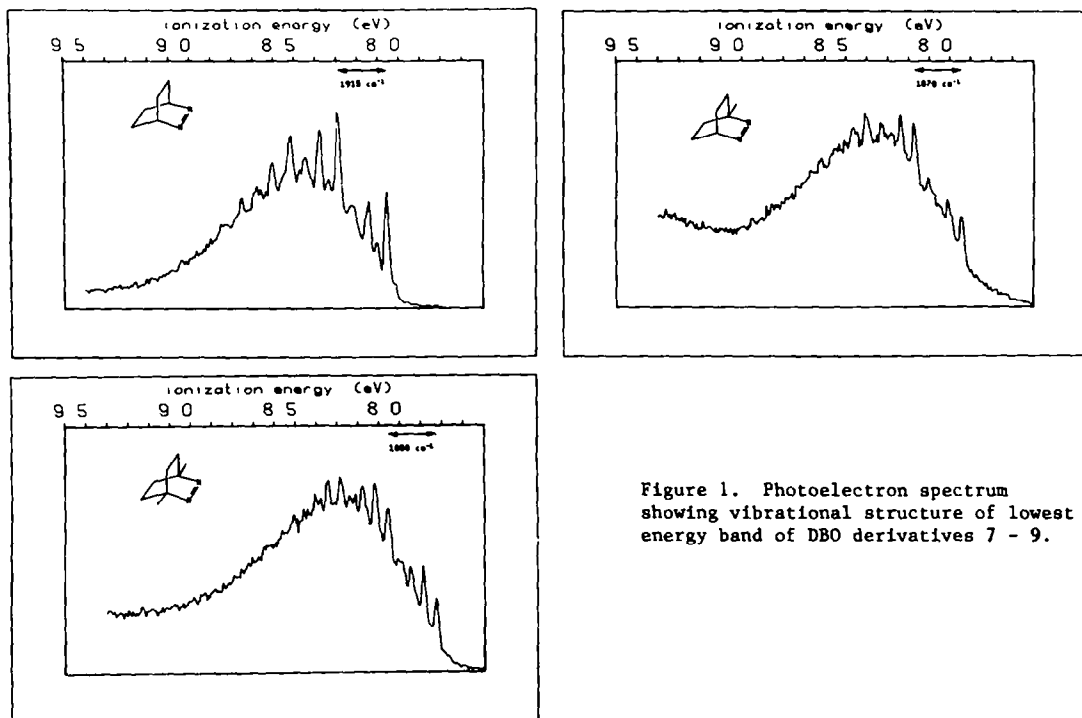


Figure 1. Photoelectron spectrum showing vibrational structure of lowest energy band of DBO derivatives 7 - 9.

The dominant vibrational progression of 7 exhibits a frequency of 1915 cm^{-1} , which must arise from the N = N stretching mode. The frequency increase relative to the 1570 cm^{-1} normally observed in the ground state²⁷ shows that the ion has a higher force constant, suggesting as in the case of diimide⁶ that an electron was removed from an antibonding orbital. It follows that the HOMO of azoalkanes is the antibonding combination of nitrogen lone pairs, in complete accord with theory.²⁶

We postulated earlier that the photochemical lability of DBO derivatives correlates with the lowest IP.^{1,28} However, the present data do not support this idea because the IP(1) of compounds 7-12 all lie between 8.06 and 8.34 eV while the deazotation rates of the excited singlet state are 4.1×10^4 , 4.0×10^4 , 4.0×10^4 , 1.8×10^9 , 4.0×10^8 , and $4.0 \times 10^5\text{ s}^{-1}$ respectively.²¹ The IP of 13 is unusually high; moreover, the effect of two α -chlorines in DBO is roughly twice the effect of one chlorine in the 1-pyrazoline series.¹

The IP(1) of 14 (8.28 eV) is comparable to that of its symmetrical counterparts azo-*tert*-butane (8.20, 8.33 eV)^{1,7} and azobenzene (8.5 eV)^{2,9} showing that conjugation of the n orbital with the benzene ring is unimportant. On the other hand, conjugation of the azo group π orbital with one benzene ring lowers IP(2) to nearly the value for azobenzene (IP(2)=8.8 eV).^{2,9}

This work brings the number of measured azoalkane ionization potentials to about 40. Unfortunately, the values do not correlate with the *cis-trans* energy difference and they are unrelated to the photochemical deazotation rates of DBO derivatives. It is likely, however, that these IP's will be useful in understanding one electron oxidation of azoalkanes.⁹⁻¹³

Experimental The PE spectra were taken on a McPherson 36 ESCA Photoelectron Spectrometer. Spectra were enhanced by signal averaging on a PDP-11 computer, yielding resolution that ranged from 12 to 20 meV. The azoalkanes were vaporized into the spectrometer at temperatures ranging from 25 to 62 °C at a pressure below 3×10^{-5} torr. All of the azoalkanes are known compounds whose preparation can be found in the references cited.

References

- Houk, K. N.; Chang, Y.-M.; Engel, P. S. *J. Am. Chem. Soc.* 1975, 97, 1824.
- Haselbach, E.; Heilbronner, E. *Helv. Chem. Acta.* 1970, 53, 684. Haselbach, E.; Schmelzer, S. *ibid* 1971, 54, 1575. *ibid* 1972, 55, 1745. Haselbach, E.; Heilbronner, E.; Mannschreck, A.; Seitz, W. *Angew. Chem. Int. Ed. Engl.* 1970, 9, 902.
- Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* 1972, 94, 1451. Robin, M. B.; Brundle, C. R.; Kuebler, N. A.; Ellison, G. B.; Wiberg, K. B. *J. Chem. Phys.* 1972, 57, 1758.
- a. Boyd, R. J.; Bunzli, J. C.; Snyder, J. P.; Heyman, M. L. *J. Am. Chem. Soc.* 1973, 95, 6478. b. Boyd, R. J.; Bunzli, J. C.; Snyder, J. P. *J. Am. Chem. Soc.* 1976, 98, 2398.
- Schmidt, H.; Schweig, A.; Trost, B. M.; Neubold, H. B.; Scudder, P. H. *J. Am. Chem. Soc.* 1974, 96, 622.
- Frost, D. C.; Lee, S. T.; McDowell, C. A.; Westwood, N. P. C. *J. Chem. Phys.* 1976, 64, 4719.
- Koenig, T.; Balle, T.; Snell, W. *J. Am. Chem. Soc.* 1975, 97, 662.
- Domelsmith, L. N.; Houk, K. N.; Timberlake, J. W.; Szilagyi, S. *Chem. Phys. Lett.* 1977, 48, 471.
- Bae, D. H.; Engel, P. S.; Keys, D. E.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* 1985, 107, 2561.
- Adam, W.; Grabowski, S.; Miranda, M. A.; Rubenacker, M. *J. Chem. Soc. Chem. Commun.* 1988, 142.
- Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* 1985, 107, 4964.
- Adam, W.; Dorr, M. *J. Am. Chem. Soc.* 1987, 109, 1570.
- Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* 1987, 109, 2484.
- Rhodes, C. J.; Louwrier, P. W. F. *J. Chem. Res.(S)* 1988, 38.
- Shine, H. J. unpublished results. Nelsen, S. F. unpublished results.
- Compounds 3c and 4c are too unstable for vaporization into the spectrometer.^{17,18}
- Chae, W. K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Ozmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* 1981, 103, 4824.
- Schmittel, M.; RÜchardt, C. *J. Am. Chem. Soc.* 1987, 109, 2750.
- Engel, P. S. *Chem. Rev.* 1980, 80, 99.
- Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* 1983, 105, 7102.
- Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* 1983, 105, 7108.
- Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* 1987, 52, 5015.
- Porter, N. A.; Funk, M. O. *J. C. S. Chem. Commun.* 1973, 263. Hinz, J.; Oberlinner, A.; RÜchardt, C. *Tetrahedron Lett.* 1973, 1975.
- Engel, P. S.; Gerth, D. B. *J. Am. Chem. Soc.* 1981, 103, 7689.
- Frisch, M. J.; Raghavachari, K.; Pople, J.; Bouma, W. J.; Radom, L. *Chem. Phys.* 1983, 75, 323.
- Baird, N. C.; Wernette, D. A. *Can. J. Chem.* 1977, 55, 350; Baird, N. C. *Can. J. Chem.* 1979, 57, 98.
- a. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds" 4th Ed. Wiley, New York, 1981, p. 130. b. Durig, J. R.; Pate, C. B.; Harris, W. C. *J. Chem. Phys.* 1972, 56, 5652. c. Spialter, L.; O'Brien, D. H.; Unterreiner, G. L.; Rush, W. A. *J. Org. Chem.* 1965, 30, 3278.
- Mirbach, M. J.; Liu, K. C.; Mirbach, M. F.; Cherry, W. R.; Turro, N. J.; Engel, P. S. *J. Am. Chem. Soc.* 1978, 100, 5122.
- Millefiori, S.; Millefiori, A.; Pignataro, S.; Distefano, G.; Colonna, F. P. *Z. Naturforsch* 1979, 34a, 1496.

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