

Correlation of Oxidation and Ionization Potentials for Azoalkanes

Werner M. Nau,^{*,†} Waldemar Adam,[§] Dieter Klapstein,[‡] Coskun Sahin,[§] and Herbert Walter[§]

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland, Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada

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Oxidation and ionization potentials of azoalkanes have been measured and combined with the available literature data to afford a data set of ten cyclic, bicyclic, and polycyclic derivatives with a wide structural variation. A linear correlation ($r = 0.939$) between the peak oxidation potentials (E_p) and the vertical ionization potentials (IP_v) of the azoalkanes **1–10** applies ($E_p = 0.95(IP_v) - 6.4$). The approximately unit slope is interpreted in terms of relatively constant differential solvation and cationic relaxation energies for the various azoalkanes. Density functional calculations (B3LYP/6-31G*) for bicyclic azoalkanes confirm that the cationic relaxation energies are relatively insensitive to molecular strain and rigidity; the latter are known to dictate their ionization potentials. The theoretical data indicate further that the preferred modes of geometry reorganization in the azoalkane radical cations are shortening of the N=N, lengthening of the C–N bonds, and widening of the C–N=N, but no torsion about the C–N=N–C dihedral angle. The experimental and theoretical data for bicyclic azoalkanes are compared with those for the corresponding bicyclic peroxide analogues.

Introduction

There is a substantial interest in correlating redox potentials in solution with experimental electron affinities^{1,2} or ionization potentials^{3–12} in the gas phase, or with theoretical heats of ionization and frontier orbital (HOMO, LUMO) energies.^{12–19} Although the solution and gas-phase measurements represent complementary techniques to assess redox properties, they are subject to various experimental limitations. This may render difficult to determine either the gas phase values, in particular the electron affinities,^{1,2} or more commonly the solution values. Hence, in the absence of experimental data, a correlation between the solution and gas phase

parameters is desirable to estimate unknown redox properties in one or the other phase. For example, most often the experimental gas phase ionization potentials for a particular class of compounds are available but only few solution oxidation potentials are at hand. The former have usually been obtained through photoelectron spectroscopy (PES), traditionally motivated by the elucidation of general relationships between electronic properties and molecular structure, while the latter are frequently required to evaluate the mechanism of electron transfer in a redox reaction.

Azoalkanes constitute a typical class of substrates for which such a dilemma between the solution oxidation and gas phase ionization potentials obtains. Through intensive PES investigations in the 1970s, which persist to date, more than 100 ionization potentials for azoalkanes have been reported,^{11,20–33} but since the one-electron

[†] Universität Basel.

[§] Universität Würzburg.

[‡] St. Francis Xavier University.

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oxidation of azoalkanes is mostly irreversible,^{34,35} only a few peak oxidation potentials have been reported.^{36–39} However, since in recent years mechanistic^{34,36–46} and spectroscopic^{35,47–53} studies on azoalkane radical cations have gained increasing attention, this unsatisfactory situation must be remedied. Hence, in the present work we introduce a convenient and useful correlation between the experimentally available oxidation and ionization potentials of azoalkanes, which allows us to estimate one if the other is known.

Results

Table 1 lists the azoalkanes for which both peak oxidation potentials (E_p) and vertical ionization potentials (IP_v) are available from the literature or from the present study. The standard cyclic voltammetric method was used to obtain six E_p values, and the previously described PES procedure³¹ was employed to measure two new values for IP_v .⁵⁴ For 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**) three independently determined peak potentials (*versus* SCE) are available, namely, 1.42,³⁶ 1.44,⁵⁵ and 1.49 V (this work), implying a typical maximum error of ± 0.07 V. For 7,7-dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**2**) two values (1.83 and 1.88 V) were also obtained with two different cyclic voltammetric setups and found to lie

Table 1. Peak Oxidation Potentials and Vertical Ionization Potentials of Azoalkanes

azoalkane	E_p^a	IP_v^b
1	1.97 ^c	8.89 ^{d,e}
2	1.85 ^c	8.70 ^f
3	1.59 ^c	8.61 ^f
4	2.1 ^g	8.74 ^{e,h}
5	1.45 ^{i,j}	8.32 ^{e,k}
6	1.34 ^l	8.13 ^{e,m}
7	1.34 ^{e,j}	8.09 ⁿ
8	2.05 ^o	8.94 ^p
9	2.3 ^q	9.05 ^q
10	1.83 ^{c,r}	8.50 ^s

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(54) The photoelectron spectrum of 1,4-dimethyldiazabicyclo[2.2.1]-hept-2-ene (**3**) exhibited vertical ionization bands at 8.61 ± 0.04 eV (adiabatic energy at 8.2 ± 0.1 eV), 10.8 ± 0.1 eV, and 11.2 ± 0.1 eV, which were assigned to ionizations from the n , $\pi(N=N)$, and $\sigma(CC)$ molecular orbitals. The spectrum of 7,7-dimethyldiazabicyclo[2.2.1]-hept-2-ene (**2**) showed vertical ionization bands at 8.59 ± 0.04 eV for n (adiabatic energy at 8.39 ± 0.04 eV), 10.7 ± 0.1 eV for $\pi(N=N)$, and 11.3 ± 0.1 eV for $\sigma(CC)$. The assignments are based on comparison with the results from related PES studies (refs 20–24 and 31) and on scaled (factor 0.92) *ab initio* calculated eigenvalues (HF/3-21G*). It is noteworthy that the spectrum of 7,7-dimethyldiazabicyclo[2.2.1]-hept-2-ene (**2**) displayed vibrational fine structure (progressions of 1610 ± 150 cm^{-1} and ca. 400 cm^{-1}). The Franck–Condon maximum of this structured band, which is given in Table 1, was found to lie at 8.70 ± 0.05 eV.

(55) G. Greiner, personal communication.

^a Peak oxidation potentials in acetonitrile *versus* SCE electrode (scan rates 0.1–0.2 V/s and 0.1 M supporting electrolyte). ^b Vertical ionization potentials. ^c This work, scan rate 100–200 mV/s. ^d References 22, 24, and 31. ^e The mean value of the available experimental data is given; for fine-structured bands,^{30,31,54} the maximum of the Franck–Condon envelope is taken, *cf.* Results. ^f This work, see also ref 54. ^g Reference 37. ^h Mean value from refs 22 and 24. ⁱ Mean value of E_p obtained in ref 36 (1.42 V), in ref 55 (1.44 V), and this work (1.49 V). ^j The values in ref 39 in methylene chloride appear to be too high (*cf.* Results). ^k Mean value from refs 24 and 30. ^l Reference 36. ^m Mean value from refs 23 and 30. ⁿ Reference 30. ^o Reference 38. ^p Reference 23. ^q Reference 21. ^r This is somewhat higher than the value previously estimated (1.70 V, ref 63) by using eq 1 and the IP_v from this table. ^s Franck–Condon maximum determined from the fine-structured band in ref 31.

within the same error limit. Of course, since the peak potentials for an irreversible oxidation process depend on the scan rate⁸ (e.g., the E_p values of the examined azoalkanes increased by ca. 50–80 mV when the scan rate was varied from 0.05 to 4 V/s) it is desirable to compare data which were obtained at the same or very similar scan rates like those in Table 1 (0.1–0.2 V/s).

The peak oxidation potentials for 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**) and its 1-phenyl derivative (**7**) were also measured in methylene chloride as solvent⁵⁶ to afford values of 1.53 and 1.39 V *versus* 1.49 and 1.34 V in acetonitrile. The slightly higher E_p values in methylene chloride, which indicate a solvent effect of ca. 0.05 V, are in contrast to recently reported data (1.69 and 1.53 V, same scan rate of 0.1 V/s), from which an unexpectedly large solvent effect would be expected in comparison with the acetonitrile data in Table 1.

The data for IP_v are also subject to various experimental uncertainties, which may include errors in reproducibility for the same instrument (typically ± 0.04 eV for our data) and errors due to different instruments, record-

(56) We thank a reviewer for drawing our attention to this point.

ing techniques, or calibration. For example, values in the range 8.83–8.96 eV have been reported in four independent measurements for 2,3-diazabicyclo[2.2.1]-hept-2-ene (**1**),^{22,24,31} which indicates a typical error of ± 0.07 eV. There may also be an error in locating the band maximum, which becomes particularly important when bands with vibrational fine structure are compared with unresolved bands. In such problematic cases, the strongest vibrational peak, which is often given as IP_v for fine-structured bands, does not necessarily coincide with the maximum of an unresolved band (Franck–Condon envelope). To illustrate, the vibrational fine structure for the lowest ionization of 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**) has been resolved in one case ($IP_v = 8.13$ eV),³⁰ but in another study an unresolved band was obtained with the maximum at 8.32 eV taken as IP_v .²⁴ Hence, in order to obtain consistent data and in agreement with literature procedures,^{11,24} the maximum of the Franck–Condon envelope was used in Table 1 even for cases with vibrational fine structure.^{30,31,54}

Discussion

A number of correlations between oxidation and ionization potentials have been established for several classes of compounds.^{3–12} Although the adiabatic ionization potentials (IP_a) are preferred for correlation⁶ since they include (as the oxidation potentials) contributions due to the geometric relaxation or reorganization energy of the cations (E_{relax}), vertical ionization potentials (IP_v) are more straightforward to determine and, hence, have been extensively used. Similarly, although it is more common to employ half-wave potentials ($E_{1/2}$),¹² linear correlations are also obtained for the peak oxidation potentials (E_p) in those cases for which $E_{1/2}$ cannot be accurately determined.^{5,7–10,19}

The present correlation for azoalkanes utilizes E_p and IP_v as characteristic data, since $E_{1/2}$ and IP_a values are not accessible in all cases.^{34–36} Despite the large variations in azoalkane structures (cyclic, bicyclic, and polycyclic) and the different sources of the data, the linear regression analysis of the data from Table 1 reveals a good linear correlation (Figure 1, $r = 0.939$). Typical error bars for the IP_v value of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1**) and the E_p value of 2,3-diazabicyclo[2.2.2]oct-2-ene (**5**), *cf.* Results, are also contained in Figure 1 to illustrate the significance of the correlation. Both the intercept (6.4) and the slope (0.95) of the regression line (eq 1) fall slightly outside the range observed for the intercept (3.4–6.2) and the slope (0.66–0.92) in previous correlations.^{3–12} Interestingly, even the only reversible oxidation potential ($E_{1/2} = 1.40$ V versus SCE; $IP_v = 8.24$)^{30,35} for azonorborene (**11**) falls very close to the regression line (triangle in Figure 1).⁵⁷

$$E_p = (0.95 \pm 0.12)(IP_v) - (6.4 \pm 1.1) \quad (1)$$

The slope of the correlation for the azoalkanes is unity within experimental error, the theoretically expected value in the absence of secondary effects. Such effects, which have been held responsible for the smaller-than-

(57) This happenstance may be fortuitous and, as noted by a reviewer, probably results from the balance of two counteracting effects, namely, the reversibility of the azonorborene oxidation, which raises its $E_{1/2}$ in relation to E_p for the irreversible oxidations of the bicyclic azoalkanes, and its acyclic structure, which allows for an extra geometric relaxation compared to the rigid cyclic derivatives **1–10** and, hence, may cause a relative lowering of $E_{1/2}$ by a similar amount.

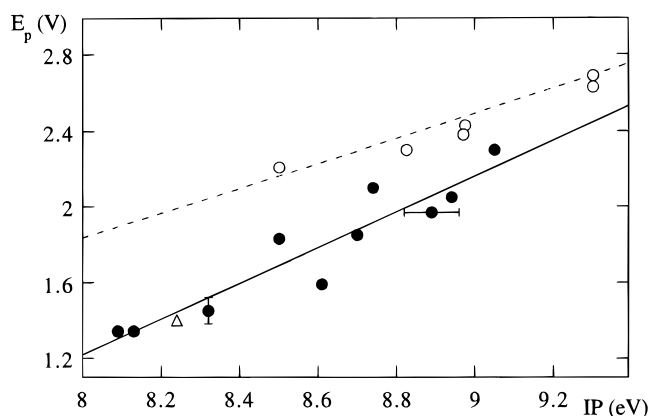
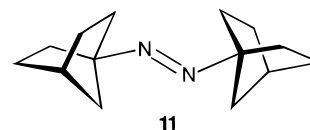


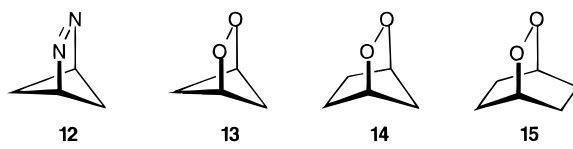
Figure 1. Peak oxidation potentials (E_p) of azoalkanes **1–10** (●) in acetonitrile from Table 1 (0.1–0.2 V/s) versus the corresponding vertical ionization potentials (IP_v) and the resulting (solid) linear regression line (eq 1). Also shown are the data derived from reversible oxidation potentials ($E_{1/2}$), namely, for bicyclic peroxides in methylene chloride⁹ (○), for azonorborene (**11**) in acetonitrile^{30,35} (Δ), and for the low-relaxation line (dashed, *cf.* text).^{9,10} To the original data of $E_{1/2}$, a small, constant value of 0.03 V was added to approximately convert the half-wave to the theoretically expected peak potentials.^{35,39}



unity slopes in previous correlations,^{3,4,8,16,17} comprise differential solvation and relaxation of the resulting cations, which are quite often dependent on the same structural characteristics as the ionization potentials. For example, in the case of correlations for aromatic substrates, the electron removal from small π systems not only requires more energy and results in a higher IP_v value but, since a more strongly bonding molecular orbital is affected, larger E_{relax} values may result. Moreover, the solvation energies are also higher due to the larger charge density in a smaller molecule.^{16,17} This results in a superimposed but systematic energy dependence on the ionization potentials, which may reduce the slope but not necessarily the linearity of a correlation between oxidation and ionization potentials.

In the case of the azoalkanes, the unit slope indicates that the above alluded secondary effects (differential solvation energies and E_{relax}) remain fairly constant regardless of the large range in the ionization potentials. Since solvation energies do not exceed a variation of 3 kcal/mol in the oxidation potentials for closely related compounds,^{8–11,35} it appears reasonable that the solvation effects for the various azoalkanes are similar. Indeed, this is intuitively expected since the size of the derivatives **1–10** in Table 1 does not vary drastically (compared to the large variations for π systems);^{3,5,16,17} moreover, the charge is expectedly localized on the azo moiety (C–N=N–C) in all cases.

In regard to E_{relax} , it was tentatively expected that the more strained derivatives should exhibit smaller E_{relax} on account of the increased molecular rigidity. Such strain and rigidity is structurally achieved through the incorporation of the azo group into smaller cyclic or bicyclic molecules. However, since the ionization potentials of azoalkanes, apart from inductive effects,²³ show as well a rapid increase with molecular strain (more

Table 2. Calculated and Experimental Vertical Ionization Potentials (IP_v) for Bicyclic Azoalkanes and Peroxides, Relaxation Energies (E_{relax}), and Geometry Changes of the Radical Cations


azoalkane or peroxide	IP _v		E _{relax}		calcd geometry changes ^{a,b}		
	calcd ^{a,c} (eV)	exptl (eV)	calcd ^{a,d} (kcal/mol)	exptl ^e (kcal/mol)	Δ(X-X) (pm)	Δ(C-X) (pm)	Δ(C-X-X) (deg)
12	9.08	9.3 ^f	8.7		-7.5	+4.4	+2.9
13	8.89		6.6		+16.2	+6.4	+3.3
1	8.66	8.89 ^g	9.4	11.8	-8.0	+10.2	+1.5
14	8.64	8.99 ^h	7.8	ca. 5.0 ⁱ	+15.8	+6.1	+3.0
5	8.03	8.32 ^g	9.3	8.5-12.2	-8.4	+11.5	+1.2
15	8.31	8.82 ^h	6.7	ca. 6.2 ^j	+14.2	+3.9	+3.1

^a The calculated data were obtained at the B3LYP/6-31G* level of theory. ^b X = N, O. The geometry changes indicate the changes of the X-X and C-X bond lengths and the C-X-X bond angle upon relaxation of the radical cation from the geometry of the neutral molecule. ^c Calculated as the energy difference between the singly ionized and neutral molecule at the optimized geometry of the neutral species. ^d Calculated as the energy difference between the radical cation at the geometry of the neutral molecule and at the fully optimized geometry. ^e Gas phase values estimated as difference between the adiabatic and vertical IP from refs 20, 30, and 62. ^f Reference 11. ^g From Table 1. ^h Reference 62. ⁱ The adiabatic potential was calculated from the experimentally observed vibrational progression (880 cm⁻¹) by assuming two progressions to reach the adiabatic peak, as indicated in the photoelectron spectrum. ^j The adiabatic potential was estimated from the spectrum (8.55 eV).

precisely with a decrease in the C-N=N angle),^{11,20-27,30,31} *cf.* also Table 1, any pronounced relationship between E_{relax} and molecular strain should reduce the slope of the correlation between E_p and IP_v significantly below unity, which is *not observed* (Figure 1). Hence, contrary to intuition, molecular strain appears to be no common denominator for E_{relax} in azoalkanes. The same conclusion was drawn from the results of density functional calculations⁵⁸ (B3LYP/6-31G*) on a series of azoalkanes, in which the molecular strain and rigidity are quite different, namely for the three simplest homologues of bicyclic azoalkanes (**1**, **5**, **12**). The theoretically computed results in Table 2, which refer to the gas phase, demonstrate indeed that E_{relax} does not vary strongly or systematically with the molecular rigidity and, hence, not with IP_v. This finding is in line with experimental values for E_{relax} of the corresponding azoalkane radical cations in the gas phase, which are quite close to the calculated values (Table 2).

Bicyclic peroxides are the dioxo analogues of the bicyclic azoalkanes in Table 1. Although the peroxide oxidation is reversible in many cases, a comparison with the azoalkane peak oxidation potentials is of interest, since the former have been employed, along with other compounds, to define a "low-relaxation" line (E_{1/2} = 0.66(IP_v) - 3.47),^{9,10} which was deemed to be characteristic for molecules, which undergo little (ca. 3 kcal/mol) geometric reorganization upon ionization. The azoalkane regression line (solid line in Figure 1) falls far below the "low-relaxation" line (dashed). For example, the bicyclic peroxides (open circles in Figure 1) have quite similar IP_v values, but their E_{1/2} values are ca. 0.3-0.5 V higher than E_p for azoalkanes.⁹

The deviation between the two data sets may be due to several reasons. Most importantly, the irreversibility of the oxidation of bicyclic azoalkanes results in a

lowering of the apparent peak oxidation potentials relative to their "true" oxidation potentials.⁸ Secondly, the relaxation energies (E_{relax}) of the azoalkanes **1**, **5**, and **12** (ca. 9-12 kcal/mol, Table 2), appear to be somewhat larger than those for the corresponding peroxides **13**-**15** (ca. 5-8 kcal/mol, Table 2, no clear-cut trend with molecular strain was recognized for the peroxides either) and the other molecules (alkylated benzenes and fused hydrocarbons) employed in the "low-relaxation" line (ca. 3 kcal/mol)^{8,9,59}. Thirdly, we note that methylene chloride has been employed as solvent for the peroxide oxidations,⁹ but acetonitrile for the azoalkane data. For the peak potentials of azoalkanes, somewhat higher E_p values are obtained in methylene chloride compared to acetonitrile. The appropriate corrections for the solvation effect (ca. 0.05 V, *cf.* Results) and for the differential relaxation effect (ca. 3 kcal/mol or ca. 0.13 V) would both tend to bring the peroxide and azoalkane data closer together, and the remaining differences (ca. 0.1-0.3 V) are supposedly due the irreversibility, since differential solvation effects are unlikely to be important for the closely related bicyclic azoalkanes and peroxides.

The question of the nature of the geometric reorganization in azoalkane radical cations needs to be addressed. Based on PES data and calculated MO energies,^{11,20-24,27,30,31} it has been agreed that the lowest-energy ionization of cyclic and bicyclic azoalkanes corresponds to removal of an electron from the antibonding n_z orbital, i.e., the antisymmetric combination of the nitrogen lone pairs. Hence, azoalkane radical cations are of the σ type, which is confirmed by ESR spectral data.^{35,47-51}

As a result of the ionization from the *antibonding* n_z orbital of the azo group, a strengthening and shortening of the N=N bond should result, which is indicated experimentally by the fine structure of the lowest PE

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(59) The noticeable divergence of the solid and dashed correlation lines in Figure 1 as IP_v decreases and the smaller than unity slope of the latter may be in part due to steadily decreasing relaxation energies along the dashed line, while E_{relax} for the azoalkanes remains relatively constant (ca. 10 kcal/mol). That the peroxide data fall on the "low-relaxation" line despite their relatively high relaxation energies (compared to the alkylated benzenes and fused hydrocarbons) may be in part due to the counteracting solvent effect (choice of methylene chloride), as was originally suspected (ref 9).

band.^{30,31,54} The vibrational progressions (1600–1950 cm^{-1}) are assigned to the N=N stretching vibration in the radical cation, which is higher in energy than that in the neutral azoalkanes (ca. 1500 cm^{-1}). Inspection of molecular models demonstrates that the required shortening of an N=N bond should be accompanied by a widening of the C–N=N angle. Both geometry changes, promoted upon ionization, are also reflected by the theoretical data for the bicyclic azoalkane derivatives **1**, **5**, and **12** in Table 2. However, the calculations further expose a significant lengthening of the C–N bonds (Table 2) which might reflect a concomitant withdrawal of electron density from, and thereby a weakening of, the C–N σ bonds. Due to the weakening of the C–N and strengthening of the N=N bonds, it is not surprising that most azoalkane radical cations prefer to denitrogenate to the hydrocarbon radical cations.^{34,36–46} It should be noted that the postulated geometry changes are fully consistent with the bond lengths determined for azoalkane-cation-like CT complexes.⁴⁷ Presumably the preferred geometric reorganization modes of the azoalkane radical cations, namely, shortening of the N=N and lengthening of the C–N bonds, are hardly encumbered by molecular rigidity; the latter may provide a rationale for the apparently constant E_{relax} values of different azoalkanes (see Discussion above).

Torsion about the C–N=N–C dihedral angle (away from the planar C–N=N–C arrangement in the neutral molecules) is the presumed mode of reorganization in azoalkane radical anions^{50,60,61} and electronically excited azoalkanes.³¹ However, neither ESR spectral evidence^{35,47–51} for azoalkane radical cations nor X-ray crystallographic data on charge-transfer complexes with positively charged azoalkanes⁴⁷ indicate any significant torsion about the C–N=N–C angle, i.e., the azo linkage remains coplanar. Such torsion or a change of the molecular symmetry upon ionization is also not suggested by the calculated geometries of the bicyclic azoalkane radical cations (Table 2), i.e., removal of symmetry constraints in the calculations preserves the coplanar arrangement.

Interestingly, although peroxide radical cations are assigned as π type,⁹ the geometry changes are very similar as for the σ type azoalkanes (Table 2). The

contraction of the O–O bond length upon ionization is, however, more pronounced than that for the N=N bond. Presumably, the introduction of double-bond character into a single bond (in the O–O bond due to ionization from an antibonding π^* MO) causes a larger effect than the introduction of triple-bond character into a double bond (in the N=N bond). The C–O–O–C dihedral, however, was also calculated to be coplanar for the three bicyclic peroxides in both the neutral and ionized molecules, although deviations from this arrangement may be possible for the higher homologues.⁶²

In conclusion, the observed linear correlation between peak oxidation potentials (E_p) and vertical ionization potentials (IP_v) for azoalkanes allows to estimate unknown or inaccessible oxidation potentials in solution. For example, one may predict from the high ionization potentials (IP_v ca. 10 eV)^{23,27} of the smallest cyclic azoalkanes, the diazirines, that their oxidation potentials are too high to measure (>3.0 V vs SCE). Another important result of this study is that the relaxation or reorganization energies of the azoalkane radical cations, which are due to shortening of the N=N bond, lengthening of the C–N bonds, and widening of the C–N=N angle, are significant (ca. 10 kcal/mol in the gas phase) but appear to be fairly constant for a wide variety of azoalkanes. Such behavior accounts for the observed unit slope of the correlation between the peak oxidation and vertical ionization potentials.

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Supporting Information Available: Optimized geometries and energies from density functional (B3LYP/6-31G*) calculations (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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