financial support of this research by the Environmental Protection Agency through Grant No. R804359. We wish to thank Professor P. D. Ellis for his helpful comments.

References and Notes

(1) For recent reviews see (a) R. A. Zingaro and W. C. Cooper, Ed., "Selenium", Van Nostrand-Reinhold, New York, N.Y., 1974, Chapter 9; (b) D. L. Klayman and W. H. H. Gunther, Ed., "Organic Selenium Compounds. Their Chemistry and Biology", Wiley-Interscience New York, N.Y., 1973, Chapter 13; (c) D. V. Frost and D. Ingrolstad, *Chem. Scr.*, **8A**, 96 (1975); (d) K. Schwartz and K. D. Pathak, *ibid.*, **8A**, 85 (1975); (e) G. N. Schrauzer, *Bioinorg. Chem.*, **5**, 275 (1976).
(2) (a) T. Birchall, R. J. Gillespie, and S. L. Vekris, *Can. J. Chem.*, **43**, 1672 (1965); (b) W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1397 (1972); (c) S. Gronowitz, I. Johnson, and A. B. Hornfeldt, *Chem. Scr.*, **8**, 8 (1975); (d) A. Fredga, S. Gronowitz, and A. B. Hornfeldt, *ibid.*, **8**, 15 (1975).
(3) H. J. Reich and J. E. Trend, *J. Chem. Soc., Chem. Commun.*, 310 (1976).
(4) E. Oldfield and A. Allerhand, *J. Biol. Chem.*, **250**, 6403 (1975), and references therein.
(5) (a) R. Ernst, *Adv. Magn. Reson.*, **2**, 1 (1966); (b) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971.
(6) (a) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect. Chemical Applications", Academic Press, New York, N.Y., 1971; (b) J. R. Lyerla, Jr., and G. C. Levy, *Top. Carbon-13 NMR Spectrosc.*, **1**, 81 (1974); (c) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1961.
(7) Samples were contained in 12-mm NMR tubes and were ~1.0 M. FTNMR spectra were recorded on a Varian Associates XL-100-15 spectrometer operating in the Gyro Observe mode at 19.1 MHz. To obtain a signal-to-noise ratio of 20:1 for the fully decoupled spectra, it was necessary to accumulate ~30 transients with a 90° flip angle.
(8) (a) M. Sass and D. Ziessow, *J. Magn. Reson.*, **25**, 263 (1977); (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972; (c) D. Canet, *J. Magn. Reson.*, **23**, 361 (1976).
(9) The NOEs were determined from the relative integrated areas of coupled and decoupled spectra. A recycle time of 7-10 T_1s was employed to enable the net magnetization to reestablish equilibrium.
(10) In this discussion we do not attempt to differentiate between the mechanisms arising from overall molecular reorientation and that due to internal motions (spin-internal rotation).
(11) C. Deverell, *Mol. Phys.*, **18**, 319 (1970).
(12) Calculated from the data in J. F. Beecher, *J. Mol. Spectrosc.*, **21**, 414 (1966).
(13) J. R. Durig and W. E. Bucy, *J. Mol. Spectrosc.*, **64**, 474 (1977).
(14) R. K. Harris and B. J. Kimber, *Appl. Spectrosc. Rev.*, **10**, 117 (1975).
(15) (a) P. S. Hubbard, *Phys. Res.*, **131**, 1155 (1963); (b) D. K. Green and J. G. Powles, *Proc. Phys. Soc. London*, **85**, 87 (1965).
(16) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).
(17) F. W. Wehrli, *Top. Carbon-13 NMR Spectrosc.*, **2**, 343 (1976).
(18) Reference 1b, Chapter 15B and references therein.
(19) (a) E. Oldfield, R. S. Norton, and A. Allerhand, *J. Biol. Chem.*, **250**, 6368 (1975); (b) W. E. Hull and B. D. Sykes, *J. Mol. Biol.*, **98**, 121 (1975).

W. H. Dawson,* J. D. Odom*
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received August 15, 1977

Structure-Energy Correlations for Hydrazine and 2-Tetrazene Oxidation Potentials

Sir:

The tetraalkylhydrazine, hydrazine radical cation redox equilibrium is electrochemically reversible (electron transfer is rapid and the cation radical long lived relative to the time scale of cyclic voltammetry experiments), allowing easy measurement of the thermodynamically significant standard potential, $E°$. $E°$ becomes more positive as it becomes more difficult to remove an electron. $E°$ values measured to ±0.01 V (0.2 kcal/mol) have been reported for a series of tetraalkylhydrazines with a variety of alkyl substituents,[1] giving a set of relative free-energy differences between radical cation and neutral hydrazine. Unlike many reversible redox equilibria, great structural reorganization takes place upon loss of an electron from a hydrazine. Neutral hydrazines have nearly tetrahedral nitrogens,[2] and there is a decided electronic preference for gauche lone pairs, so that, even with rather large alkyl groups, the lone pair-lone pair dihedral angle remains near 90° in the absence of N_1,N_2 bridging.[3] The radical cations are best described as "three electron pi-bonded" structures, and have olefin-like geometries, but the ease of bending at nitrogen is considerably greater than the case of bending at the carbons of an olefin, and the equilibrium geometry is sometimes nonplanar at nitrogen, although activation energies for double nitrogen inversion are quite low.[4] As a consequence of the geometrical change upon electron removal, a hydrazine radical cation has increased $R-N_1N_2-R$ steric interaction relative to that of the neutral hydrazine. When a bulky enough alkyl group is attached to nitrogen, like a *tert*-butyl group, this increase in $R-N_1N_2-R$ strain becomes dominant, and $E°$ increases sharply. Nevertheless, there is a measurable decrease in $E°$ upon *N*-alkyl group homologation, and even upon introduction of α branching by inclusion of isopropyl substituted compounds.[1] For real understanding of the $E°$ values observed for tetraalkylhydrazines, it is necessary to be able to separate the steric and electronic effects observed upon changing alkyl group.

Table I. $E°$ Values (V vs. SCE, in Acetonitrile Containing 0.1 M Sodium Perchlorate) for Some Tetraalkylhydrazines and Tetraalkyl-2-tetrazenes

Substitution	Hydrazine I	2-Tetrazene II
$R_i = CH_3$	0.28[a]	0.41
$R_1 = R_3 = CH_3CH_3$; $R_2 = R_4$ CH_3	0.26[a]	0.36
$R_i = CH_2CH_3$	0.24[a]	0.33
$R_i = CH_2CH_2CH_3$	0.24[a]	0.31
$R_i = CH_2CH_2CH_2CH_3$	0.24[a]	0.30
$R_i = HC(CH_3)_2$		0.23
$R_1 = CH_2Ph$; $R_2 = R_3 = R_4 = CH_3$	0.35	
$R_1 = R_2 = CH_2Ph$; $R_3 = R_4 = CH_3$	0.44	
$R_1 = R_3 = CH_2Ph$; $R_2 = R_4 = CH_3$	0.43	0.51
$R_i = CH_2Ph$	0.60	0.59

[a] From ref 1, where the other saturated alkyl compounds plotted in Figure 1 are also tabulated.

The idea that the electron-releasing effect of alkyl substituents increases with homologation and α branching was expressed quantitatively in terms of σ^* constants by Taft[5] and, as Shorter has pointed out, is rather firmly ingrained in the thinking of organic chemists.[6] The effects are not particularly large, and Ritchie has shown that, for some systems, Taft correlations work as well when σ^* is assigned as zero for simple alkyl groups.[7] Inversions in the σ^*-predicted order are also known, as Brauman and Blair[8] showed for the vapor phase acidity of alkyl alcohols and as Bordwell and coworkers[9] demonstrated in solution for 9-fluorenes with a CH_2, S, or SO_2 interposed between the ring and the alkyl group. The idea that detectable differences in "electronic effects" by different saturated alkyl groups are present in solution at all has been challenged by Charton,[10] who restudied ester and amide hydrolysis data extensively, concluding that the Taft assumption of identical steric effects in acid and base catalyzed ester hydrolysis which led to Taft's σ^* evaluation is frequently wrong, that σ^* values do not reflect differences in electrical effects, but, rather, involve steric factors, and that alkyl groups do not differ significantly in their electrical effects.[10a] We have seen one reply to Charton's arguments which focused on methodology in data treatment.[11]

We report here data indicating that alkyl groups do indeed show a detectable difference in their ability to stabilize dialkylamino radical cations relative to the neutral compounds in solution, and that σ^* does give a useful linear correlation with alkyl electronic effects. For any test of the value of σ^* in quantitatively indicating alkyl group electronic effects, benzyl

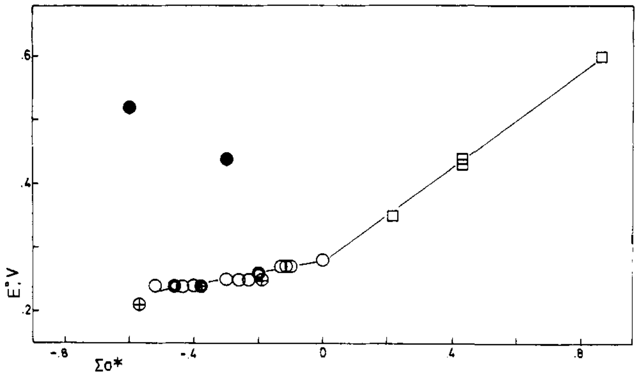


Figure 1. $E°$ vs. $\Sigma\sigma^*$ plot for some tetraalkylhydrazines: ○, *n*-alkyl compounds (ref 1, compounds **1–14**); ⊕, isopropyl, methyl substituted (ref 1, compounds **15–18**); ●, *tert*-butyltrimethyl and 1,2-di-*tert*-butyl-1,2-dimethyl (ref 1, compounds **19** and **20**); □, benzyl, methyl (Table I).

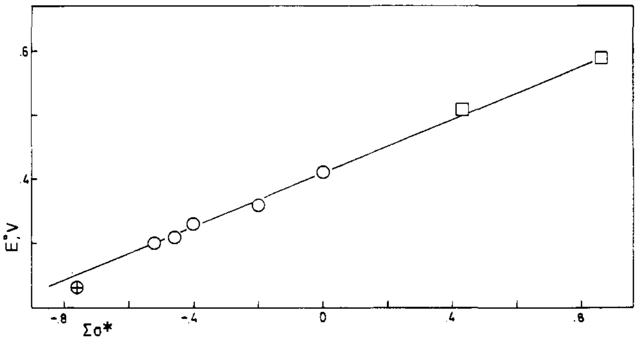
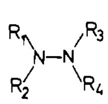
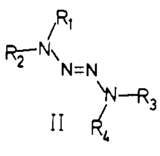


Figure 2. $E°$ vs. $\Sigma\sigma^*$ plot for the 2-tetrazenes of Table I.

seemed to us to be a crucial group to include, because it has the opposite sign for σ^* as saturated alkyl groups, eliminating the parallelism of Taft steric and electronic effects which has been emphasized by Charton.[10] A positive slope for an $E°$ vs. $\Sigma\sigma^*$ plot is expected, because a less electron-releasing alkyl group (more positive σ^*) should cause an electron to be removed less easily (more positive $E°$). Including data for benzylated hydrazines (see Table I) causes a sharp break in the Taft plot (Figure 1), which is roughly linear if either *n*-alkyl or benzyl, methyl substituted compounds are considered separately. Because benzyl is large, in addition to being electron withdrawing relative to methyl, perhaps the reason for the break in the correlation of Figure 1 is not a breakdown in Taft's σ^* values, but simply steric, benzyl raising $E°$ for the same reason that *tert*-butyl does. To test this hypothesis, $E°$ values for some



I



II

tetraalkyl-2-tetrazenes (II) were determined. There is a clear structural analogy between I and II, and the formal charge at the dialkyl nitrogen is nearly as high in $II^{+\cdot}$ as in $I^{+\cdot}$ (the dialkyl nitrogen ESR splitting constants for the tetramethyl cations are 13.1[4] and 10.9[12] G, an admittedly imperfect but highly indicative experimental measure of charge density for these systems). The key difference between I and II oxidation is the fact that little steric strain will be introduced upon flattening at the dialkylamino groups of II, in contrast to the case for I. As shown in Figure 2, the effect of alkyl group homologation upon $E°$ is significantly greater for II than for I, and the Taft plot is linear, including both *n*-alkyl[13] and benzyl substituted tetrazenes. These results indicate that $E°$ values for even tetra-*n*-alkylhydrazines are quite detectably influenced by steric differences, but that the electronic effect of changing alkyl group size is somewhat larger in magnitude.[14] Work intended to quantitatively separate the steric and electronic effects of alkyl group substitution upon I oxidation, using II as a model, is currently in progress.[15]

References and Notes

(1) S. F. Nelsen, V. Peacock, and G. R. Weisman, *J. Am. Chem. Soc.*, **98**, 5269 (1976).

(2) (a) For a review of hydrazine conformational work to 1973, see Y. Shvo, "The Chemistry of Hydrazo, Azo, and Azoxy Groups", Part 2, S. Patai, Ed., Wiley, New York, N.Y., 1975, pp 1017–1095. (b) For recent structural work showing that the degree of flattening at nitrogen depends slightly upon the lone pair–lone pair dihedral angle, see S. F. Nelsen, W. C. Hollinsed, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 4461 (1977).

(3) S. F. Nelsen and J. M. Buschek, *J. Am. Chem. Soc.*, **96**, 2311, 5282, 5287 (1974), and references therein.

(4) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Am. Chem. Soc.*, **96**, 2916 (1974).

(5) R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13.

(6) J. Shorter, *Adv. Linear Free Energy Relat.*, Chapter 2, 99 (1972).

(7) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).

(8) J. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970).

(9) F. G. Bordwell, G. E. Drucker, and G. J. McCollumn, *J. Org. Chem.*, **41**, 2786 (1976).

(10) (a) M. Charton, *J. Am. Chem. Soc.*, **97**, 3691 (1975); (b) M. Charton, *ibid.*, **99**, 5687 (1977).

(11) A.-J. MacPhee and J.-E. Dubois, *Tetrahedron Lett.*, 2471 (1976).

(12) W. M. Tolles, D. W. Moore, and W. E. Thun, *J. Am. Chem. Soc.*, **88**, 3476 (1966).

(13) The downward deviation for tetraisopropyl-2-tetrazene apparent in Figure 2 might also be caused by a steric effect, release of R_1NR_2 interaction upon flattening at nitrogen. Experiments to elucidate this point are underway.

(14) Solvation effects are clearly of great importance in ionic reactions, as work like that of ref 8 shows. It is clear from IP_v data in the vapor phase that a far greater sensitivity to alkyl group homologation and α branching is observed in the absence of solvent.[1] Although σ^* values do a good job of quantitatively correlating the size of the effect for hydrazines, a better correlation is obtained by comparing one set of photoelectron spectroscopy data with another; see B. J. Cocksey, D. H. Eland, and W. Danby, *J. Chem. Soc. B*, 790 (1971). The solvation effect seems quite nonspecific for tetraalkylhydrazine oxidation, because the same $E°$ patterns are observed for solvents as different as acetonitrile and methylenene chloride.[1]

(15) We thank the National Science Foundation for partial financial support of this work.

S. F. Nelsen,* V. E. Peacock
Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706

Received August 4, 1977

Synthesis of $(CH_3)_4C_4B_4H_4$. An Example of Photochemical Addition of an Alkyne to a Borane via a Ferraborane Intermediate

Sir:

The production of carboranes from alkyne-boron hydride mixtures under various reaction conditions is well known.[1] However, carboranes containing other than two carbons are relatively rare.[2] In an examination of the electronic structure of some ferraboranes, similarities (and differences) were noted between the structures of $B_4H_8Fe(CO)_3$ and $C_4H_4Fe(CO)_3$.[3] Pettit has shown[4] that reactions between cyclobutadiene and unsaturated molecules coordinated to iron take place readily. Coordination of the unsaturated molecule to iron apparently occurs after the photolytic ejection of a carbon monoxide molecule from cyclobutadiene iron tricarbonyl. In the case of alkynes, this is followed by cycloaddition. An analogous reaction with the ferraborane would produce a carborane. Herein is reported evidence for the formation of two new carboranes by the photolysis of $B_4H_8Fe(CO)_3$ in the presence of 2-butyne. As the ferraborane itself is prepared by the direct reaction of $Fe(CO)_5$ and B_5H_9,[5] two readily available compounds, this constitutes a convenient route to these carboranes.

Irradiation at 254 nM of a bright orange solution of 0.6 mmol of $B_4H_8Fe(CO)_3$ and 20 mmol of 2-butyne in 2.8 mL of diethyl ether for 17 h in a Rayonet photochemical reactor resulted in a dark solution and the production of 1.8 mmol of