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Ionization from Nitrogen and Oxygen Lone Pairs: A Comparison of Trialkylamine, Dialkyl Ether, Tetraalkylhydrazine, and Dialkyl Peroxide Photoelectron Spectroscopic Ionization Potentials

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Danby's μ_R parameter for predicting ionization potential (IP) when alkyl groups are changed is applied to complex cyclic as well as simple alkyl groups, and comparisons are made for 112 examples of the title compounds. Ring size and RNR angle, as well as RNN angle and lone pair, lone pair dihedral angle in hydrazines, all affect IP very noticeably. In contrast, ether and peroxide IP values are quite insensitive to the analogous parameters. This is argued to result from the difference in lone pair hybridization, which is about sp^3 for unstrained amino nitrogen, and pure p for ether oxygen.

Introduction

Larger alkyl groups are well-known to decrease the ionization potentials of heteroatomic compounds relative to smaller ones. Danby and co-workers[1] showed that vertical ionization potentials (IP$_v$) could be described empirically by using substituent parameters μ_R ($\mu_{Me} = 0$, μ_R is negative for larger alkyl groups) with eq 1. We wish

$$\mathrm{IP_v(RX)} = \mathrm{IP_v(MeX)} + m'\mu_R \qquad (1)$$

to consider extending such correlations to cyclic compounds for which μ_R is not defined; the alkyl groups Danby and co-workers considered were only attached to the heteroatom at a single point. We believe it is convenient to think of μ_R values in terms of the "effective number of carbons" in the alkyl group, n_{eff}, as defined in eq 2. The

$$n_{eff} = 1 + \frac{\mu_{(R)}}{\mu_{(Et)}} \qquad (2)$$

one carbon methyl group is the reference and can be assigned any value of the substituent parameter, and the difference between the methyl and ethyl parameters can also be assigned independently by changing m'. Although using n_{eff} instead of μ_R is a trivial change, it allows easy direct comparison of the effect of enlarging the alkyl group (see Table I). Introduction of a second and third β carbon in comparing *i*-Pr and *t*-Bu to Et causes a noticable saturation effect, as discussed previously.[2] Comfortingly, introduction of a γ carbon causes the same change in n_{eff} in *n*-Pr (vs. Et) and *t*-Pe (vs. *t*-Bu). The fall off in Δn_{eff} for the first β, γ, δ, and ϵ carbons is 1.00, 0.48, 0.25, and 0.06. Taft reported over 25 years ago[3] that the drop off in observed solution "inductive effect" was 0.45 for introducing a methylene group "insulating" a substituent from the test center. The factor of 0.45 per CH$_2$ group introduced would lead to values of 1.00, 0.45, 0.20, and 0.09 for the above series, very close to the observed values. It is now accepted that the IP$_v$ lowering effect of alkyl group homologation in the vapor phase is principally a result of increasing the ease of alkyl group polarization.[4] The n_{eff} values seem to represent simple counting up of α, β, γ, δ, and ϵ carbons, allowing for a saturation effect when more than one is present. This can obviously be done for complex alkyl groups with more than one point of attachment to the heteroatom. In this paper, we consider cyclic as well as acyclic alkyl substituents and contrast their effect upon substitution at nitrogen and oxygen atoms, which show important differences.

Table I. n_{eff} Values for Simple Alkyl Groups

group	n_c[a]	n_{eff}	notes
Me	1	1.00	reference alkyl group
Et	2	2.00	first β carbon, 1.00
i-Pr	3	2.87	second β carbon, 0.87
t-Bu	4	3.64	third β carbon, 0.77
n-Pr	3	2.48	first γ carbon, 0.48
t-Pe	5	4.13	first γ carbon, 0.49
i-Bu	4	2.94	second γ carbon, 0.46
n-Bu	4	2.73	first δ carbon, 0.25
i-Pe	5	2.90	second δ carbon, 0.17
n-Pe	5	2.79	first ϵ carbon, 0.06

[a] Number of carbons in the alkyl group.

Table II. Comparison of Observed and Calculated (eq 3) Average IP Values for Tri-*n*-alkylamines

compd	IP$_{av}$[a]	Dev[a]	compd	IP$_{av}$	Dev
1, Me$_3$N[b]	8.53[c]	−0.01	14 (H)	8.06[f]	−0.03
2, Et$_2$MeN[b]	8.44[c]	+0.03	14 (Me)	8.06[f]	+0.01
3, *n*-BuMe$_2$N[b]	8.35[d]	+0.04	14 (Et)	8.05[f]	0.00
4, *i*-BuMe$_2$N[b]	8.31[d]	+0.03	14 (*i*-Pr)	7.99[f]	−0.04
5, Et$_2$MeN[b]	8.22[c]	−0.06	14 (*t*-Bu)	7.97[f]	−0.06
6, Et$_3$N[b]	8.08[c]	−0.07	15	7.94[g]	+0.02
7, *n*-Pr$_3$N[b]	7.92[c]	0.00	16	7.84[h]	−0.03
8, *n*-Bu$_3$N[b]	7.90[c]	+0.04	17	7.13[j]	−0.88
9, (CH$_2$)$_4$NMe	8.41[e]	0.00	18 (Me)	7.84[k]	−0.09
10, (CH$_2$)$_5$NMe	8.29[e]	−0.05	18 (Et)	7.76[k]	−0.04
11, (CH$_2$)$_6$NMe	8.92[e]	+0.01	18 (*n*-Pr)	7.71[k]	−0.03
12, *i*-PrMe$_2$N	8.20[d]	−0.09	18 (*i*-Pr)	7.68[k]	0.00
13, *t*-BuMe$_2$N	8.08[d]	−0.11	18 (*t*-Bu)	7.30[k]	−0.29
			19	8.68[e]	+0.39

[a] Units eV, in this and all subsequent tables. [b] Used in determining eq 3. [c] From ref 5. [d] Determined by Glen Cunkle, previously unpublished. [e] From ref 6. [f] From ref 7. [g] From ref 8. [h] From ref 9. [j] From ref 10. [k] From ref 11.

Trialkylamine IP$_v$ Values. Experimental data determined by five groups[5-10] are presented in Table II. As

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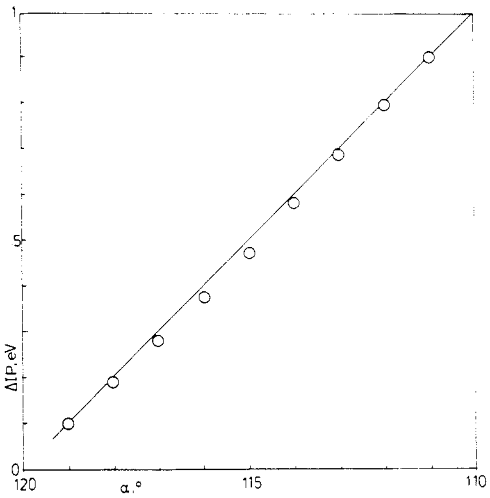
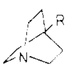


Figure 1. Comparison of calculated (MNDO and FOGO) ΔIP = IP(α) − IP(α = 120°) vs. α with a linear relationship (ΔIP was normalized to 1.0 at 110°).

expected a Danby plot, IP_v vs. n_{eff}, of the n-alkyl substituted examples 1–8 is a rather good straight line, giving eq 3. Values of Dev (see eq 4), the deviation of the experimental IP_v values from that predicted by eq 3 are also listed in Table II. The average |Dev| for 1–8 is 0.03 eV, which is probably about the size of the experimental error in measuring IP_v. Structures for the polycyclic entries in Table II are shown below (**14**–**19**). Table II shows that

$$I_{calcd}(R_3N) = 8.92 - 0.12_9\sum n_{eff} \qquad (3)$$

$$Dev = IP_v - I_{calcd} \qquad (4)$$


14(R)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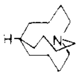
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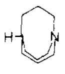
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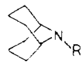
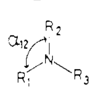

18(R)


19

cyclic, bicyclic, and tricyclic alkyl group effects on IP_v are properly represented simply by using n_{eff}, because **9**–**11**, **14(H)**–**14(*t*-Bu)**, and **15** show small Dev values (average |Dev| for these compounds is 0.02_4, no larger than that for the n-alkyl compounds). Importantly, the above examples were chosen because their cyclic and bicyclic alkyl groups do not significantly change the bond angles at the nitrogen atom. It has already been noted several times that when the substituents do change bond angles at nitrogen, IP_v is affected substantially. Small rings (such as in aziridine **19**) close one RNR angle α, increasing the s character of



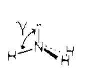


Table III. Comparison of Geometry at Nitrogen by Allinger MM2 Calculations and Equation 5

compd	α_{av} (by MM2)	α_{est} (eq 5)
12, i-$PrMe_2N$	111.1	111.7
13, t-$BuMe_2N$	112.2	111.9
16	112[a]	111.1
18 (Me)	111.7	111.7
18 (Et)	111.7	111.2
18 (n-Pr)	111.8	111.1
18 (i-Pr)	112.0	110.8
18 (t-Bu)	114.4	113.8

[a] From ref 9, MM1 calculation.

Table IV. Comparison of IP_{av} Values for Ethers with Equation 6

compd	IP_{av}	Dev
20, Me_2O	9.94[a]	+0.05
21, $(CH_2)_3O$	9.63[b]	−0.09
22, Et_2O	9.50–9.55[a,c]	−0.05 to 0.00
23, $(CH_2)_4O$	9.57[c]	+0.02
24, $(CH_2)_5O$	9.46[d]	−0.01
25, i-Pr_2O	9.30–9.35[c]	+0.04 to 0.09
26, n-Pr_2O	9.32[a]	−0.07
27	9.12[e]	+0.03
28, t-Bu_2O	8.95[a]	−0.05

[a] Reference 1. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19.

the lone pair and causing a large rise in IP_v.[6] Increasing the angle α flattens the nitrogen, causing decreases in IP_v.[9-11] We suggest that since a reasonably quantitative measure of how much the geometry changes have affected IP_v is now available in Dev, one ought to be able to use this to measure rehybridization of the nitrogen lone pair. It was pointed out that MINDO/3 calculations on NH_3 with varying degrees of flattening gave a nearly linear IP_v vs. f_p plot, where f_p is the fractional p orbital character of the nitrogen lone pair.[11] Along similar lines, Alder, Heilbronner, and co-workers[9] have presented a plot of FOGO[12] calculated IP_v vs. γ for NH_3. MNDO[13] calculated IP_v vs. γ for NH_3 has almost exactly the same shape as the FOGO calculation, although the calculated ΔIP at γ = 110° (increase in IP_v from the value at γ = 90° (pure p lone pair)) is 0.94 eV by FOGO and 1.08 eV by MNDO. Figure 1 has a plot of ΔIP_v vs. α for NH_3 by both FOGO and MNDO, rescaled to give an arbitrary ΔIP_v of 1.0 eV at α = 110°. It is very close to linear, and we suggest the Dev should be experimentally linear with α_{av}. Trimethylamine has an α_{av} of about 110.8°.[14] It is generally accepted that **17** is planar at nitrogen,[9,10] giving an experimental value for the Dev of a planar trialkylamine, and since α_{av} changes 9.2° between the bent trimethylamine and a planar nitrogen, we suggest the relationship between the calculated value of α_{av}, α_{est}, and Dev shown in eq 5. Unfortunately,

$$\alpha_{est} = 110.8 - 9.2Dev/0.88 \qquad (5)$$

few structural data on trialkylamines are available to test eq 5. Allinger's MM2 molecular mechanics calculation[15] does reproduce α_{av} for Me_3N, and although it is known to fail badly for very flattened nitrogens like that of **17**,[9] we compare MM2 calculated α_{av} values with α_{est} values from eq 5 in Table III. Branched alkyl compounds **12** and **13** were included because their Dev values are slightly more negative than the n-alkyl compounds. Although almost as much flattening is predicted by MM2 as by α_{est} for t-$BuMe_2N$, the Dev value for i-$PrMe_2N$ is more negative than MM2 predicted it should be (by 0.6° in α). Little flattening is predicted by a MM1 calculation for **16**,[9] and Dev is small. MM2 does predict a much greater flattening at N for **18**(t-Bu) than the smaller substituents, but there is a downward drift in α_{est} (less negative Dev) in the series

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Table V. Comparison of IP_{av} Values for Unbranched Acyclic and 1,1-Alkylene-2,2-dialkylhydrazines with Equation 7

compd	IP_{av}, eV	Dev, eV	compd	IP_{av}, eV	Δ, eV	Dev, eV
30, Me_2NNMe_2	8.5^a	+0.01	**45**, $(CH_2)_4NNMe_2$	8.41	0.62	+0.05
31, $EtMeNNMe_2$	8.45^a	0.00	**46**, $(CH_2)_4NN(CH_2)_4$	8.19	0.56	0.00
32, EtMeNNMeEt	8.34^a	−0.02	**47**, $(CH_2)_5NNMe_2$	8.36	0.54	+0.04
33, Et_2NNMe_2	8.37^a	+0.01	**48**, $(CH_2)_5NN(CH_2)_4$	8.23	0.55	+0.08
34, $Et_2NNMeEt$	8.27^a	−0.01	**49**, $(CH_2)_5NN(CH_2)_5$	8.15	0.52	+0.05
35, Et_2NNEt_2	8.20^a	+0.01	**50**, $(CH_2)_6NNMe_2$	8.22	0.62	−0.06
36, n-$PrMeNNMe_2$	8.40	−0.01	**51**, $(CH_2)_6NN(CH_2)_4$	8.12	0.64	+0.02
37, n-Pr_2NNMe_2	8.24	−0.04	**52**, $(CH_2)_6NN(CH_2)_5$	8.17	0.59	+0.11
38, n-Pr_2NNEt_2	8.13	+0.03	**53**, $(CH_2)_7NNMe_2$	8.20	0.65	−0.06
39, n-Pr_2NN-n-Pr_2	8.07	+0.05				
40, n-$BuMeNNMe_2$	8.32	−0.07				
41, n-Bu_2NNMe_2	8.23	0.00				
42, n-Bu_2NNEt_2	8.03	−0.03				
43, n-Bu_2NN-n-Bu_2	7.93	0.00				
44, n-$Heptyl_2NNMe_2$	8.21	-0.01^b				

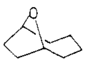
[a] Used in calculating eq 6. [b] Carbons past the ϵ carbons were ignored; $n_{eff} = 7.58$ was used.

18(Me) to 18(i-Pr) which is certainly not caused sterically (as the slight increase in α_{av} calculated by MM2 in this series shows). Although the differences are small enough to be on the order of experimental error in measuring Dev, these data could also be a result of alkyl group anisotropy, a point we will return to below. The MM2 α_{av} and α_{est} values are encouragingly close for 18(t-Bu). Additional data, both photoelectron spectroscopic and structural, have to be collected before the validity of eq 5 can really be tested properly.

Ether IP_v Values. Danby and co-workers[1] included four ethers in their original μ_R correlation, and other literature ether IP_v values[16–19] are also collected in Table IV. Although there is more scatter than in the trialkylamine data, all of these ethers show a reasonable fit to the linear regression line, eq 6, with an average |Dev| of about 0.05

$$I_{calcd}(R_2O) = 10.22 - 0.16_8 n_{eff} \qquad (6)$$

eV. There is not a significant negative increment in Dev for α branching, as is observed for alkylated amino nitrogen compounds. Both **25** and **28** show rather large (Dev) values but they are in opposite directions. Although oxetane **21** has a large Dev of −0.09, a positive increment in Dev is certainly not observed for closing the ROR angle in a 4-membered ring, as it is for amino nitrogen compounds.[6] Ethylene oxide (IP_v = 10.57[16]) clearly does show a positive increment in IP_v compared to less strained compounds. **27** has a small Dev, but **29** (IP_v = 9.50–9.55 eV[17]) has a large Dev (+0.24 to 0.29). Hoffmann, Mollère, and Heilbronner[17] have pointed out that this should not be considered a bond angle contraction effect, but an interesting consequence of orbital symmetry; **29** is a very special case which should not be expected to fit on an IP_v vs. n_{eff} plot.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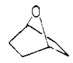
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We will take up the question of why amino nitrogen and ether oxygen compounds show different behavior in IP_v vs. n_{eff} plots at the end of the paper.

Tetraalkylhydrazine IP_{av} Values. To extend IP–n_{eff} comparisons to tetraalkylhydrazines, it is necessary to deal with the fact that hydrazines have two lone pair dominated ionization potentials, which have a separation $\Delta = IP_2 - IP_1$ which is sensitive to the lone pair, lone pair dihedral angle θ. Although approximate MO calculations predict Δ to vary approximately as $\cos\theta$,[2,20] and Δ to go to zero at a θ value somewhat less than 90° (83° for MINDO/3 calculations on Me_2NNMe_2 with tetrahedral nitrogens), this clearly does not appear experimentally, as a host of compounds with gauche lone pairs have $\Delta = 0.53 \pm 0.03$ eV. We presume there is an avoided crossing, making Δ insensitive to θ near about 85°.[21] Hydrazines with θ near 180° and 0° show Δ near 2.3 eV. We will correlate $IP_{av} = (IP_2 + IP_1)/2$ with n_{eff}. IP_{av} may be thought of as representing the lone pair energy with (hypothetical) absence of splitting between the symmetric and antisymmetric lone pair combination orbitals. Using the six Me or Et substituted compounds **30–35** gives eq 7, with a maximum Dev

$$I_{calcd}(R_2NNR_2) = 8.99_1 - 0.08_8 \sum n_{eff} \qquad (7)$$

of 0.02 eV, (Table V). As required from the earlier comparison of IP_1 with μ_R,[21] the nine n-alkyl hydrazines with larger substituents also correlate well, and the average |Dev| for **36–44** is 0.03 eV. As expected from the trialkylamine data, inclusion of compounds with five- to eight-membered rings shows only slightly more scatter; **45–53** have an average |Dev| of 0.05 eV. Several of these compounds have a Δ value outside the 0.53 ± 0.03 range of **30–44**, but most of these are unsymmetrical ones so that the lone pairs are of different energy even before mixing. It is not obvious that any of **45–53** have θ values significantly outside the range for **30–44**; some of them might.

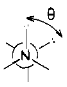

Table VI contains data for branched alkyl hydrazines. It will be noted that **56** to **59**, which have two i-Pr groups or a methyl and a $tert$-butyl group on the same nitrogen, show significant negative Dev values (−0.12 to −0.20 eV). We attribute this to sterically imposed spreading of the RNR angle. Interestingly, β branching leads to modestly positive Dev values when there are i-Bu or neo-Pe groups on adjacent nitrogens (Dev values of +0.09 to +0.25 are seen for **61, 63, 64,** and **66**). We previously suggested that this could be caused by an alkyl group anisotropic effect.

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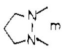
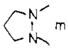
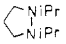
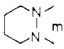
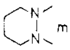
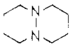
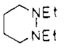
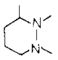
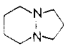
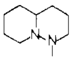
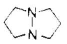
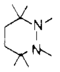
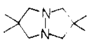
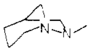
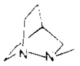
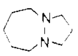
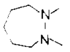
Table VI. Comparison of IP_{av} Values for Branched Alkyl Acyclic Tetraalkylhydrazines with Equation 6

compd	IP_{av}, eV	Δ, eV	Dev, eV	compd	IP_{av}, eV	Δ, eV	Dev, eV
54, *i*-PrMeNNMe$_2$	8.36	0.53	−0.01	60, *i*-BuMeNNMe$_2$	8.35	0.55	−0.02
55, *i*-PrMeNNMe-*i*-Pr	8.18	0.52	−0.03	61, *i*-BuMeNNMe-*i*-Bu	8.30	0.54	+0.10
56, *i*-Pr$_2$NNMe$_2$	8.01	0.72	−0.20	62, *i*-Bu$_2$NNMe$_2$	8.23	0.51	+0.03
57, *i*-Pr$_2$NNMe-*i*-Pr	7.90	0.60	−0.15	63, *i*-Bu$_2$NN-*i*-BuMe	8.17	0.54	+0.14
58, *t*-BuMeNNMe$_2$	8.19	0.59	−0.12	64, *i*-Bu$_2$NN-*i*-Bu$_2$	8.11	0.53	+0.25
59, *t*-BuMeNNMe-*t*-Bu	7.93	0.51	−0.14	65, neo-PeMeNNMe$_2$	8.37	0.58	+0.03[a]
				66, neo-PeMeNNMe-neo-Pe	8.16	0.62	+0.09[a]

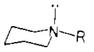
[a] Using n_{eff} for neo-Pe estimated as 0.36 larger than that for *i*-Bu.

Table VII. Comparison of IP_{av} Values for 5- to 7-Membered Ring 1,1-Alkylene-2,2-dialkylhydrazines with Equation 6

compd	IP_{av}, eV	Δ, eV	Dev, eV	compd	IP_{av}, eV	Δ, eV	Dev, eV
67a  major	8.93	2.30	+0.48	67b  minor	8.74	0.81	+0.29
				68 	8.50	0.88	+0.22
				69 	8.31	0.89	+0.19
70a  major	8.88	2.26	+0.52	70b  minor	8.27	1.04	−0.09
71 	8.76	2.31	+0.57	72 	8.15	0.67	−0.04
				73 	8.31	0.95	+0.02
74 	8.66	2.32	+0.51	75 	8.22	1.04	+0.06[b]
75 	8.66	1.51	+0.30	77 	7.56	0.99	−0.11
78 	8.64	2.21	+0.44	79 	8.51	0.65	+0.19
				80 	8.28	0.51	−0.04
81 	8.46	1.76	+0.23	82 	8.15	0.54	−0.17

[a] Only a small amount of the conformation was observed, and the numbers quoted are significantly less accurate than most of the data. [b] Using n_{eff} as the sum of Me, Et, *n*-Pr, and *i*-Pr.

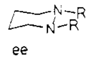
MINDO/3 calculations predict a modest sensitivity for IP_v of $EtNH_2$ to the $C_\alpha C_\beta$,N lone pair dihedral angle ψ.[21b] The



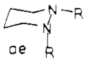
A

lowest IP_v was calculated for the ψ = 180° conformation, and the highest for $\psi \cong 65°$. β-Branching would be expected to favor gauche ψ conformations in tetraalkylhydrazines. Now that we can compare cyclic compounds to acyclic ones, we are in a better position to look for ψ effects, because piperidine rings exist in the R equatorial conformation A, enforcing gauche ring ψ values. If there really is a significant dependence of IP_v on ψ for amino nitrogen atoms, it will show up in IP vs. n_{eff} plots, in which the piperidine ring is treated as equivalent to nonoriented ethyl and *n*-propyl groups. We note that for *N*-methylpiperidine **10**, Dev was −0.05 (Table II), and that for the 5- to 7-membered ring hydrazines **45–52**, the ones containing the six-membered rings (**47**, **48**, **49**, and **52**) have an average Dev of +0.07 while the ones lacking six-membered rings (**45**, **46**, **50**, and **51**) have a average Dev of 0.00. We conclude a ψ effect may indeed be present for hydrazines, although it might be admitted it is not large compared to our experimental scatter.[22] The ψ effect appears to be small enough to ignore in our subsequent discussion.

The five- to seven-membered ring cyclic 1,2-alkylenehydrazine data are collected in Table VII. Large Δ values are caused by θ being near 180° or 0° in some conformations of these compounds. Both 1,2-dimethylpyrazolidine (**67**) and 1,2-dimethylhexahydropyradizine (**70**) show PE peaks for two conformations and hence give two entries in Table VII. The hexahydropyridazine derivatives **70–75** give the best documented case for a large θ (and hence Δ) effect on Dev. The large Δ compounds shown at the left of Table VII, **70a**, **71**, and **74**, are in the diequatorial alkyl group conformations ee, with θ ~180°, while those on the



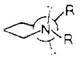
ee



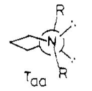
ae

right, **70b**, **72**, **73**, and **75**, are in equatorial, axial alkyl group conformations ae. There is an unmistakable difference in Dev for the ee conformations (Dev +0.51 to 0.57) and ae conformations (Dev −0.09 to +0.06). The boat hexahydropyridazine **80** has both Δ and Dev in the range of the acyclic compounds of Table V, verifying that twisting θ to unusual values is responsible for the large Dev values for the ee conformations.

The pyrazolidine derivatives show qualitatively similar behavior to the hexahydropyridazines. The major conformation of the dimethyl compound (**67a**) has Δ = 2.30 and must be in the T_{ee} conformation.[23] It has a Dev of



T_{ee}



T_{aa}

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[22] There are anomalies in the conformational behavior of *N*-ethyl compared to *N*-methyl six-ring nitrogen compounds which might also be attributed to a ψ effect, but we will not go into this very different type of discussion here.

Table VIII. Comparison of IP_{av} Values for Bicyclic α-Branched Tetraalkylhydrazines with Equation 6

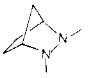
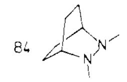
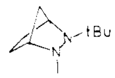
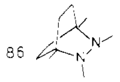
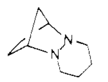
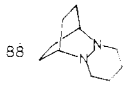
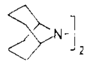
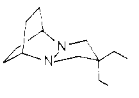
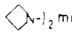
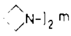
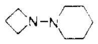
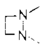
compd	IP_{av}, eV	Δ, eV	Dev, eV	compd	Δ, eV	IP_{av}, eV	Dev, eV
83 	8.54	1.78	+0.26	84 	8.37	1.82	+0.16
85 	8.32	1.95	+0.27	86 	8.16	1.46	+0.09
87 	8.25	2.11	+0.14	88 	8.08	2.29	+0.18
90 	8.01	2.13	+0.30	89 	8.21	2.32	+0.08
91 	ca. 8.54	ca. 2.02	ca. 0.41				

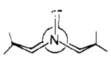
Table IX. Comparison of IP_{av} Values for Four-Membered Ring Hydrazine with Equation 6

large Δ conformations				small Δ conformations			
compd	IP_{av}, eV	Δ, eV	Dev, eV	compd	Δ, eV	IP_{av}, eV	Dev, eV
92a  minor	ca. 9.16	ca. 1.9	ca. +0.8	92b  major	8.62	0.72	+0.26
93 	8.78	2.04	+0.55	94 	8.61	0.67	+0.16
96 	9.14	2.04	+0.60	95 	8.35	0.65	+0.16

+0.48, almost as large as observed for ee hexahydropyridazines. **67b**, **68**, and **69** are in smaller Δ conformations which we assign[23] as T_{aa}, and show only modestly large Dev values (+0.19 to ca. +0.29). Bicyclic pyrazolidine **79** also has a small Δ but Dev of +0.19. The T_{aa} pyrazolidines clearly show larger Dev values than the ae hexahydropyridazines. One factor may be that their θ values are rather different. θ for ae is below the crossover point, about 60–70°, while θ for T_{aa} is above it. Angle restriction may also be a factor, for the NNC angles in pyrazolidines are held to significantly smaller values that those in hexahydropyridazines, and smaller α should raise IP. There also could be inductive raising of IP, for there are only three carbons bridging the nitrogens, and n_{eff} ignores the possibility of inductive effects.

The bicyclo[3.3.0]octyl pyrazolidines **76** and **78** are known to be in cis lone pair conformations, and the smaller

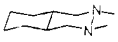
76



78

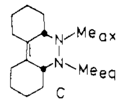
Δ for **76** shows it to have a significant θ value (we estimated 30°[23]), while the large Δ for **78** indicates it is in the θ = 0° conformation because of the methyl groups forcing envelope five-membered ring conformations. The Dev values of **76** and **78** are of intermediate size.

In trialkylamines, large positive Dev values are only seen for compounds with an α restriction which increases s character in the lone pair relative to acyclic compounds. X-ray structural work on ee hexahydropyridazine (B) and



B

α_{av} = 107.5°
$d_{NN} = 1.48_6$ Å



C

α_{av} = 111.6° (110.9 at NMe_{ax})
(112.2 at NMe_{eq})
$d_{NN} = 1.45_0$ Å

ae tetrahydropyridazine (C)[24] is significant in rationalizing the increase in Dev for ee compounds, because they reveal that rehybridization of the lone pair has occurred, despite the fact that there is no obvious steric reason for it. It is likely that the interpretation of Dev for hydrazines of different θ values is quite complex. The average lone pair orbital energy calculated at different θ values varies slightly, even when α_{av} is held constant; INDO calculations on Me_2NNMe_2 with tetrahedral nitrogens gave average lone pair energies of −11.6 eV at 90°, −11.8 at 0°, and −12.2 at 180°.[2] Another complication is that the weaker NN σ bond will be more subject to rehybridization than the CN bonds, so changes in the CNC and CNN angles ought to have different degrees of importance. The sensitivity of IP_{av} to flattening at hydrazine nitrogen ought also to be somewhat different than that at amine nitrogen. The ΔDev calculated from eq 5 in going from α_{av} of 107.5 to 112.2 is 0.44 eV, 0.72 times as large as the observed Dev difference between **70a** and **70b**.

Sterically imposed flattening at nitrogen will tend to increase p character and lower Dev even in compounds with large Δ values, and we believe there is excellent evidence for this in the α-branched 1,2-bicyclic hydrazines shown in Table VIII. Despite rather large Δ values for **83**–**91**, their Dev values are significantly less positive than for α-unbranched systems, which ought to be contributed to by sterically imposed flattening at nitrogen. For example, **87** and **88** show Δ values over 2 eV but quite modest Dev values. Despite the fact that they are ee hexahydropyridazines, restriction of the bicyclic ring CN,NC dihedral angle forces flattening at nitrogen relative to **70a**, **71**, and **74**,[25] and although Δ remains nearly as large Dev is significantly decreased.

Data for four-membered ring hydrazines[26] appear in Table IX. Here α restriction and possible inductive IP raising ought to, and in fact, does raise Dev relative to the

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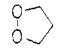
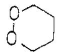
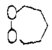
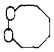
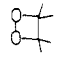
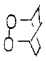
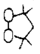
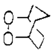
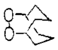
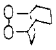
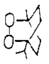
[23] Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6987.

[24] Nelsen, S. F.; Hollinsed, W. C.; Calabrese *J. Am. Chem. Soc.* **1977**, *99*, 4461.

[25] Nelsen, S. F.; Hollinsed, W. C.; Grezzo, L. A.; Parmelee, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 7347.

[26] Nelsen, S. F.; Peacock, V. E.; Weisman, G. R.; Landis, M. E.; Spencer, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 2806.

Table X. Comparison of IP_{av} Values for Peroxides with Equation 8

compd		IP_{av}	Δ	Dev
97	MeOOMe	10.66^a	1.90	0.02
98		10.50^a	1.27	0.06
99		10.26^a	0.18	0.03
100		$10.11^{b,c}$	$2.30,^b 2.24^c$	0.06
101		10.05^b	0.59	-0.8
102		9.95^b	1.31	-0.08
103		9.96^d	1.96	0.09
104	iPrOOiPr	9.94^b	1.55	0.07
105		$9.83^{b,c}$	$2.00,^b 2.02^c$	-0.04
106		$9.83,^e 9.87^d$	$1.15,^e 1.21^e$	-0.04
107		9.67^b	1.40	-0.11
108		9.56^c	0.86	-0.11
109		$9.57,^c 9.54^b$	$1.01,^c 0.98^b$	-0.13 (av)
110		9.56^d	0.41	0
111	tBuOOtBu	$9.70,^d 9.62^e$	$1.74,^d 1.68^e$	0.10 (av)
112		9.43^d	1.86	0.06

[a] Reference 29. [b] Reference 31. [c] Reference 30. [d] Reference 28. [e] Reference 30.

five- to seven-membered ring examples in Table IX. From its large Δ value, **96** is presumably in conformation **96a**.

96a

Dialkyl Peroxide IP_{av} Values. Reported PE data[27-31] for 16 dialkyl peroxides are summarized in Table X. The principal difference in the Δ vs. θ curve for hydrazines and peroxides is that the orbital crossing which is avoided for hydrazines (minimum Δ 0.53 ± 0.03 eV) must at least nearly occur for peroxides, since Δ for **99** is 0.18 eV. The maximum Δ for peroxides is about as large as for hydrazines since **100** has a Δ of 2.24 or 2.03 eV.[30,31] It will be seen in Table X and its plot in Figure 3 that deviations from the least-squares IP_{av} vs. $\sum n_{eff}$ line (eq 8) are rather

$$I_{\text{calcd}}(\text{ROOR}) = 11.06 - 0.02_6\sum n_{\text{eff}} \qquad (8)$$

larger for peroxides (average Dev = 0.07 eV) than for the other compounds discussed. Dioxetane **103** (IP_{av} = 9.96) gives only a slightly higher IP_{av} than the acyclic **104** (IP_{av} = 9.94) and bicyclic **105** (IP_{av} = 9.83) of the same n_{eff} value, so the ring size effect to be rather small. A rather low sensitivity to Δ is shown by the similarity of IP_{av} for **110** (IP_{av} = 9.56) and **111** (IP_{av} = 9.62 or 9.70), despite their large difference in Δ. The scatter in the peroxide plot of Figure 3 is clearly far smaller than in the hydrazine plot of Figure 2.

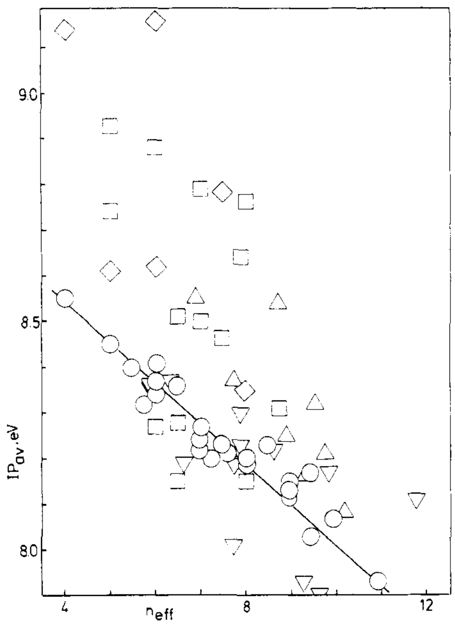


Figure 2. Plot of IP_{av} vs. n_{eff} for tetraalkylhydrazines. The line is eq 7. ○ Acyclic and cyclic 1,2-alkylene (Table V); ▽ branched acyclic (Table VI); □ cyclic 1,2-alkylene (Table VII); △ bicyclic α-branched (Table VIII); ◇ four-membered ring (Table IX).

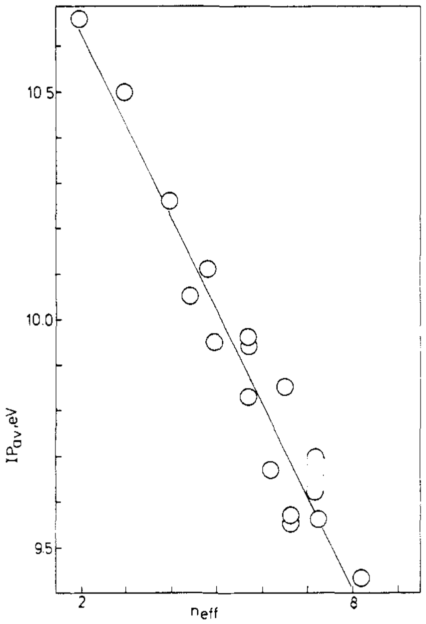


Figure 3. Plot of IP_{av} vs. n_{eff} for dialkyl peroxides. The line is eq 8.

Because IP_2 for peroxides involves ionization from an MO dominated by combinations of n orbitals which are perpendicular to the π lone pair, its energy would be expected to depend on ROO angle, and hence ring size, as well as on the RO,OR dihedral angle. The observed small sensitivity of IP_{av} to Δ and ring size presumably has a rather complex origin, which we would not have predicted. Nevertheless, the IP_{av} vs. n_{eff} plot for peroxides empirically resembles that for ethers in showing a low sensitivity to ring size and differs greatly from that for hydrazines in that the sensitivity to Δ is small.

The slopes of the IP_{av} vs. n_{eff} lines of eq 3, 6, 7, and 8 compare the sensitivities of these compounds to changes in $\sum n_{eff}$. The observed slopes are ROOR, -0.29; ROR, -0.17; R_3N, -0.13; R_2NNR_2, -0.09. The principal factor seems to be the number of alkyl groups available to stabilize the positive charge of the radical cation, although

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[27] Batich, C.; Adam, W. *Tetrahedron Lett.* **1974**, 1467.

[28] Brown, R. S. *Can. J. Chem.* **1975**, *53*, 3439.

[29] Rademacher, P.; Ellig, W. *Liebigs Ann. Chem.* **1979**, 1473.

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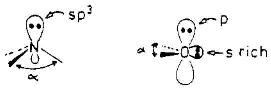
[31] Couglin, D. J.; Brown, R. S.; Salomon, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 1533.

the electron-withdrawing effect of an electronegative oxygen substituent on the adjacent oxygen in ROOR compared with ROR appears to raise the sensitivity to alkyl group stabilization.

Comparison of Alkyl Group Effects on Ionization from Oxygen and Nitrogen Lone Pairs. The principal differences observed between the oxygen- and nitrogen-containing compounds are that the nitrogen compounds show sensitivity to the degree of α-branching, ring size, and, in hydrazines, the size of θ (which is reflected in Δ). This contrast is shown graphically for hydrazines and peroxides in the IP_{av} vs. n_{eff} plots of Figures 2 and 3, respectively. Neither ether nor peroxide IP values are raised much by having four-membered rings present, while amines and hydrazines are. There is no evidence for a significant inductive effect operating through the alkyl chain in the four-membered ring oxygen compounds.

We suggest that the principal reason for the dichotomy in behavior is the difference in hybridization of the lone pairs being ionized. A nitrogen lone pair of unstrained amines and hydrazines is near sp^3 in hybridization, while



the high energy lone pair of an oxygen atom is a pure p hybrid.[32,33] The sp^3 nitrogen lone pair hybridization is sensitive to α. In contrast, the oxygen p lone pair cannot mix with the RO bonds, which lie in the p orbital nodal plane, so its energy is very insensitive to α. The energy of the s rich lone pair is sensitive to changes in α, but the first ionization involves the p lone pair.

For hydrazines, Dev is extremely sensitive to θ, the best documented difference being seen for hexahydropyridazine derivatives, where the $\theta \sim 180°$ ee conformations have a Dev of 0.54 ± 0.03 eV, and the $\theta \sim 60$–$70°$ conformations have a Dev of about 0 ± 0.09 eV. This effect is very much smaller, if present, for peroxides. IP_{av} for t-BuOO-t-Bu **111** is only 0.06 or 0.14 eV higher than for the six-membered ring analogue **110**, which differ in θ substantially (their Δ values differ by 1.4 eV, about as much as those for ee and ae hexahydropyridazines). The lone pairs of the hydrazines are mixed with the NN σ bond orbitals, so the destabilizing lone pair,lone pair interaction in $\theta \sim 0$, 180° conformations can be decreased by increasing p character in the NN bond (lengthening it) and increasing s character in the lone pair orbitals (bending more at nitrogen, decreasing α).

Conclusion

Alkyl group effects on the ionization potentials for ether oxygen and amino nitrogen are correctly predicted by the simple expedient of counting up carbons, using n_{eff}, in cases where sterically induced rehybridization has not occurred. Knowing what the IP would be in the absence of rehybridization allows determination of how much the geometry change induced by having complex alkyl substitution with more than one site of attachment to the heteroatoms has changed the ionization potentials. IP_{av} for ethers and peroxides are very insensitive to changes in α and θ, but amines and hydrazines show easily detected deviations in IP with alkyl group structure. The reason for this difference in behavior is argued to be the difference in hybridization of the lone pair being ionized. It is suggested that Dev values can be valuable in estimating α values for amino nitrogen compounds, although the situation for hydrazines is quite complex, and considerably more structural work will need to be done to understand the observed Dev values more fully.

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Registry No. **3**, 927-62-8; **4**, 7239-24-9; **12**, 996-35-0; **13**, 918-02-5; **16**, 75197-24-9; 18 (Me), 491-25-8; 18 (Et), 64776-29-0; 18 (n-Pr), 73320-99-7; 18 (i-Pr), 64776-33-6; 18 (t-Bu), 64776-36-9; **30**, 6415-12-9; **31**, 50599-41-2; **32**, 23337-93-1; **33**, 21849-74-1; **34**, 50599-43-4; **35**, 4267-00-9; **36**, 60678-65-1; **37**, 52598-09-1; **39**, 60678-69-5; **40**, 52598-10-4; **41**, 60678-67-3; **42**, 60678-68-4; **43**, 60678-70-8; **44**, 68970-10-5; **45**, 53779-90-1; **46**, 18389-95-2; **47**, 49840-60-0; **48**, 49840-66-6; **49**, 6130-94-5; **50**, 60678-76-4; **51**, 60678-75-3; **52**, 60778-60-1; **53**, 68970-11-6; **54**, 49840-63-3; **55**, 60678-71-9; **56**, 60678-72-0; **57**, 49840-64-4; **58**, 60678-73-1; **59**, 52291-46-0; **60**, 68970-04-7; **61**, 68970-05-8; **62**, 60678-74-2; **63**, 68970-06-9; **64**, 68970-07-0; **65**, 68970-08-1; **66**, 68970-09-2; **67a**, 38704-89-1; **68**, 22825-58-7; **69**, 38704-87-9; **70a**, 26163-37-1; **71**, 3661-15-2; **72**, 60678-82-2; **73**, 38704-92-6; **74**, 5721-43-7; **75**, 67318-95-0; **76**, 5397-67-1; **77**, 60678-80-0; **78**, 2940-98-9; **79**, 70873-23-3; **80**, 6523-29-1; **81**, 49840-69-9; **82**, 49840-68-8; **83**, 14287-89-9; **84**, 14287-92-4; **85**, 42842-99-9; **86**, 59498-94-1; **87**, 72282-74-7; **88**, 72282-72-5; **89**, 23211-28-1; **90**, 62796-83-2; **91**, 60678-79-7; **92a**, 67092-91-5; **93**, 67092-90-4; **94**, 67092-88-0; **95**, 67092-89-1; **96**, 52433-27-9.

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(32) (a) This assignment has always been common practice in the PE literature. Organic chemists tend to like to write two sp^3 hybridized lone pairs,[33] but Jorgensen and Salem[32b] have pointed out that the assignment used here is necessary whenever energies are to be considered. (b) Jorgensen, W. L.; Salem, L. "The Organic Chemists Book of Orbitals"; Academic Press: New York, 1973; p 42.

(33) (a) Kirby, A. J. "The Anomeric Effect and Related Stereoelectronic Effects at Oxygen"; Springer-Verlag: Berlin, 1983. (b) Deslongchamps, P. "Stereoelectronic Effects in Organic Chemistry"; Pergamon: New York, 1983.