

method B of Grunwald and Effio.<sup>10</sup> As pointed out by these workers,<sup>16</sup> the Onsager theory is likely to give an accurate result for the dipole moment of the solute (subscript 2) in self-associated solvents (subscript 1) if  $\mu_2^2/V_2 \gg \mu_1^2/V_1$ , where  $V$  denotes the molar volume. This condition is satisfied in the present case.

$V_2$  and the molar refraction  $R_2$  used in the calculation were as follows: for LiCl,  $V_2 = 10.4 \text{ cm}^3/\text{mol}$  and  $R_2 = 9.37 \text{ cm}^3/\text{mol}$ ; for KTs,  $V_2 = 121.0 \text{ cm}^3/\text{mol}$  and  $R_2 = 46.34 \text{ cm}^3/\text{mol}$ . These values were measured in acetic acid.<sup>35</sup>

### Appendix

Refer to Figure 3. The electrical center 0 is placed at an arbitrary point joining the positive point charge  $Q_p$  to the negative point charge  $Q_n$ . We are interested in the potential  $\varphi$  at any point P. It is assumed that the distances  $s$ ,  $r$ ,  $s'$  are substantially greater than  $r_p$  and  $r_n$ . The potential  $\varphi$  is given by eq 13. On applying the law

$$\varphi = (Q_p/s) + (Q_n/s') \quad (13)$$

of cosines we evaluate  $s$  and  $s'$  according to eq 14. On

$$s = (r^2 + r_p^2 - 2rr_p \cos \theta)^{1/2} \quad (14a)$$

$$s' = (r^2 + r_n^2 + 2rr_n \cos \theta)^{1/2} \quad (14b)$$

expanding in power series and neglecting terms of

(35) L. E. Mayer and C. D. Brown, unpublished results, 1970.

order  $(r_p/r)^2$ ,  $(r_n/r)^2$ , and higher, we obtain eq 15. On

$$s^{-1} = r^{-1}(1 + (r_p/r) \cos \theta + \dots) \quad (15a)$$

$$(s')^{-1} = r^{-1}(1 - (r_n/r) \cos \theta + \dots) \quad (15b)$$

substituting these expressions in eq 13, we obtain eq 16.

$$\varphi = \frac{Q_p + Q_n}{r} + \frac{(Q_p r_p + |Q_n| r_n) \cos \theta}{r^2} \quad (16)$$

To obtain eq 5a for cations, we rewrite eq 16 in the form of eq 17a. It thus becomes clear that the electrical center must be placed so that  $r_p = 0$ . To obtain eq 5 for anions, we similarly write eq 17b and place the elec-

$$\varphi_+ = \frac{Q_p + Q_n}{r} + \frac{|Q_n|(r_p + r_n) \cos \theta}{r^2} + \frac{(Q_p - |Q_n|)r_p \cos \theta}{r^2} \quad (17a)$$

$$\varphi_- = \frac{Q_p + Q_n}{r} + \frac{Q_p(r_p + r_n) \cos \theta}{r^2} + \frac{(|Q_n| - Q_p)r_n \cos \theta}{r^2} \quad (17b)$$

trical center so that  $r_n = 0$ .

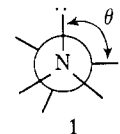
## Photoelectron Spectra of Hydrazines. III. Evidence for Similar Lone Pair-Lone Pair Dihedral Angles for Acyclic Hydrazines

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**Abstract:** The photoelectron spectra of 22 alkylated hydrazines (including six monoalkyl and nine tetraalkyl) having Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, and *t*-Bu alkyl substituents are reported. Calculations by the INDO method on the five methylated hydrazines, using a lone pair-lone pair dihedral angle ( $\theta$ ) of  $90^\circ$  correlate well with the observed IP's for these compounds (least squares (LS) line has standard deviation of 42 meV). Assuming  $\theta = 90^\circ$  for all compounds, and using a simple method to estimate the change in IP caused by replacement of methyl by another alkyl group, the plot of observed *vs.* calculated ( $\theta = 90^\circ$ ) IP for all the alkylhydrazines studied has a slope of 0.98 and an intercept of 0.15 eV, and the standard deviation is 78 meV. Since the calculations indicate a change of  $\geq 30$  meV for each degree change in  $\theta$  within  $\pm 30^\circ$  of the crossover point of the symmetric and antisymmetric lone pair MO's, it is argued that only rather small changes in  $\theta$  can be resulting from changes in alkyl substitution in these acyclic hydrazines.

The photoelectron spectra (pes) of hydrazines are of particular interest because of the presence of two "lone pair" orbitals on nitrogen, which would ionize at the same potential except for interactions of these orbitals with other orbitals and with each other. With adjacent lone pairs, one would expect the principal interaction to be the lone pair-lone pair interaction, which should be strongly dependent upon the dihedral angle between the lone pairs,  $\theta$  (see 1).<sup>1</sup> Both we<sup>2</sup> and Rademacher<sup>3</sup> have recently described pes of hydrazines

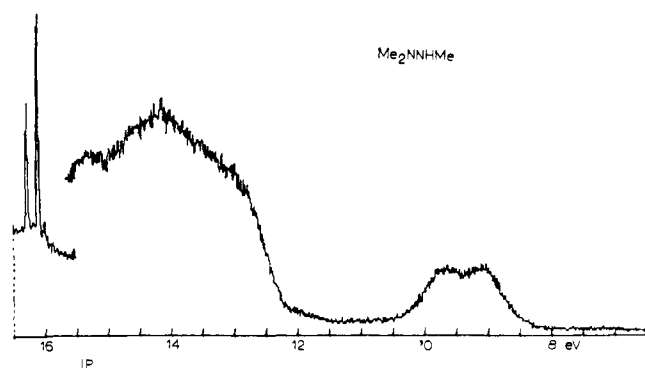


which demonstrate that this is the case. Rademacher proposed a method to evaluate the angle  $\theta$ , using the pes splitting  $\Delta$  ( $IP_2 - IP_1$ , where  $IP_1$  and  $IP_2$  are the first and second ionization potentials, attributable to "lone pair" ionizations).<sup>3</sup> To accurately describe the effects of conformation on the observed splittings, it is necessary to evaluate the magnitude of other effects, such as substitution pattern and changes in substituent groups, upon the pes. A convenient starting point for such an

(1) For a discussion of electron pair interactions in saturated molecules, see R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) (a) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (b) *ibid.*, **95**, 2013 (1973).

(3) P. Rademacher, *Angew. Chem.*, **85**, 410 (1973).



**Figure 1.** A typical acyclic hydrazine pes spectrum, that of trimethylhydrazine, 10 eV scan. The scale of eV is only approximate, and internal argon (the doublet at the left) was used for calibration.

evaluation is the analysis of the spectra of acyclic hydrazines, several of which we report here.

## Results and Discussion

The pes results for a series of 22 acyclic hydrazines are presented in Table I. All potentials reported are ver-

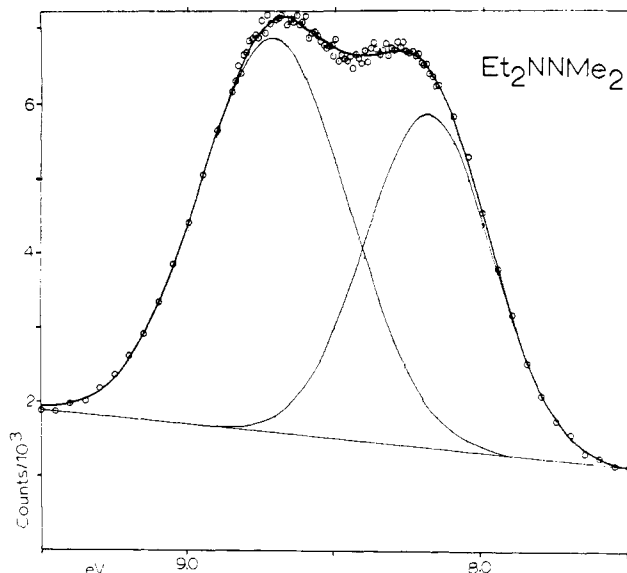
**Table I.** First and Second Vertical Ionization Potentials for Some Acyclic Hydrazines

Compd	No.	IP <sub>1</sub> , eV	IP <sub>2</sub> , eV	Δ, eV	IP <sub>av</sub> , eV
H <sub>2</sub> NNH <sub>2</sub>	2	9.90	10.75	0.85 <sub>0</sub>	10.32 <sub>5</sub>
MeHNNH <sub>2</sub>	3	9.32	10.24	0.93 <sub>0</sub>	9.78 <sub>0</sub>
EtHNNH <sub>2</sub>	4	9.20	10.14	0.94 <sub>0</sub>	9.67 <sub>0</sub>
<i>n</i> -PrHNNH <sub>2</sub>	5	9.07	10.10	1.03 <sub>0</sub>	9.58 <sub>5</sub>
<i>i</i> -PrHNNH <sub>2</sub>	6	9.05	10.00	0.95 <sub>0</sub>	9.52 <sub>5</sub>
<i>n</i> -BuHNNH <sub>2</sub>	7	9.04	9.98	0.94 <sub>0</sub>	9.51 <sub>0</sub>
<i>t</i> -BuHNNH <sub>2</sub>	8	8.92	9.95	1.03 <sub>0</sub>	9.43 <sub>5</sub>
Me <sub>2</sub> NNH <sub>2</sub>	9	8.88	10.13	1.24 <sub>6</sub>	9.50 <sub>5</sub>
<i>n</i> -Pr <sub>2</sub> NNH <sub>2</sub>	10	8.51	9.77	1.25 <sub>5</sub>	9.14 <sub>0</sub>
MeHNNHMe	11	9.00	9.73	0.72 <sub>6</sub>	9.36 <sub>5</sub>
<i>i</i> -PrHNNH- <i>i</i> -Pr	12	8.59	9.36	0.77 <sub>0</sub>	8.97 <sub>5</sub>
Me <sub>2</sub> NNHMe	13	8.67	9.34	0.66 <sub>6</sub>	9.00 <sub>5</sub>
Me <sub>2</sub> NNH- <i>i</i> -Pr	14	8.52	9.15	0.63 <sub>4</sub>	8.83 <sub>0</sub>
Me <sub>2</sub> NNMe <sub>2</sub>	15	8.27	8.83	0.55 <sub>3</sub>	8.55 <sub>0</sub>
Et <sub>2</sub> NNEt <sub>2</sub>	16	7.94	8.45	0.51 <sub>2</sub>	8.19 <sub>5</sub>
Et <sub>2</sub> NNMe <sub>2</sub>	17	8.10	8.63	0.52 <sub>4</sub>	8.36 <sub>5</sub>
Et <sub>2</sub> NN( <i>n</i> -Pr) <sub>2</sub>	18	7.87	8.39	0.52 <sub>0</sub>	8.13 <sub>0</sub>
Me- <i>t</i> -BuNN- <i>t</i> -BuMe	19	7.67	8.17	0.50 <sub>7</sub>	7.92 <sub>0</sub>
Me <sub>2</sub> NNMeEt	20	8.18	8.72	0.53 <sub>2</sub>	8.45 <sub>0</sub>
Me <sub>2</sub> NNMe- <i>n</i> -Bu	21	8.12	8.65	0.53 <sub>7</sub>	8.38 <sub>5</sub>
Me <sub>2</sub> NNMe- <i>i</i> -Pr	22	8.09	8.63	0.53 <sub>1</sub>	8.36 <sub>0</sub>
<i>i</i> -Pr <sub>2</sub> NN- <i>i</i> -PrMe	23	7.59	8.20	0.61 <sub>0</sub>	7.89 <sub>5</sub>

tical IP's (peak maxima), which have been corrected by deconvolution of the observed spectra into a pair of (overlapping) Gaussian peaks,<sup>4</sup> using a nonlinear least-squares best fit. Deconvolution is necessary because the broad peaks observed (widths at half-height are usually 0.5–0.6 eV) are seriously overlapped.<sup>5</sup> Examples of observed and deconvoluted spectra are shown in Figures 1 and 2. Comparing hydrazine with its methylated derivatives (3, 9, 11, 13, 15), a decrease in ionization potential for each methyl group was observed, as has been previously noted by Dewar and co-

(4) Using program GFIT, written by D. Lichtenberger, University of Wisconsin.

(5) The peak potentials Rademacher reports agree closely with our observed spectra before deconvolution. In two cases, *sym*-disopropylhydrazine and 1,2-diazacyclopentane (pyrazolidine), we disagree substantially; Professor Rademacher has informed us that his data were in error.



**Figure 2.** A typical deconvoluted spectrum, the lone pair region of *uns*-diethyldimethylhydrazine. The experimental data are shown as the circles (only every fifth data channel is plotted except near the maxima), superimposed on the two Gaussian peaks into which the spectrum was resolved, and their sum.

workers<sup>6</sup> for hydrazines and as is typically observed when hydrogens are replaced by methyls in other systems. The effect of homologation of an alkyl substituent can be seen by comparing compounds 3–8. The value of IP<sub>av</sub> decreases in the order Me > Et > *n*-Pr > *i*-Pr > *n*-Bu > *t*-Bu (from 9.78 to 9.44 eV). This effect has also been observed for several types of compounds, the most directly comparable case being alcohols, for which IP<sub>1</sub> decreases in the same order<sup>7</sup> (from 10.85 to 10.23 eV). The splitting Δ ought to be the most sensitive feature of the pes to variation in θ. We observed that the splittings occur in the order *uns* disubstituted (Δ ~ 1.25 eV) > monosubstituted (Δ ~ 0.95) > *sym* disubstituted (Δ ~ 0.75) > trisubstituted (Δ ~ 0.65) > tetrasubstituted (Δ ~ 0.53). The splitting is rather constant among compounds of a given substitution pattern.

For hydrazine<sup>8,9</sup> and methylhydrazine,<sup>9</sup> *ab initio* calculations indicate that θ is near 90°, in agreement with far-infrared<sup>10</sup> and microwave<sup>11</sup> results. It is clearly impractical to carry out energy minimized calculations of any sort on all of the hydrazines we have investigated. We carried out INDO calculations on hydrazine (2) and tetramethylhydrazine (15) in "standard geometry" (see Experimental Section), varying θ between 0 and 180°. The energies thus obtained are dis-

(6) N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, *Tetrahedron*, **26**, 4109 (1970). Their ionization potentials differ slightly from ours, but their instrument had a severe base-line problem.

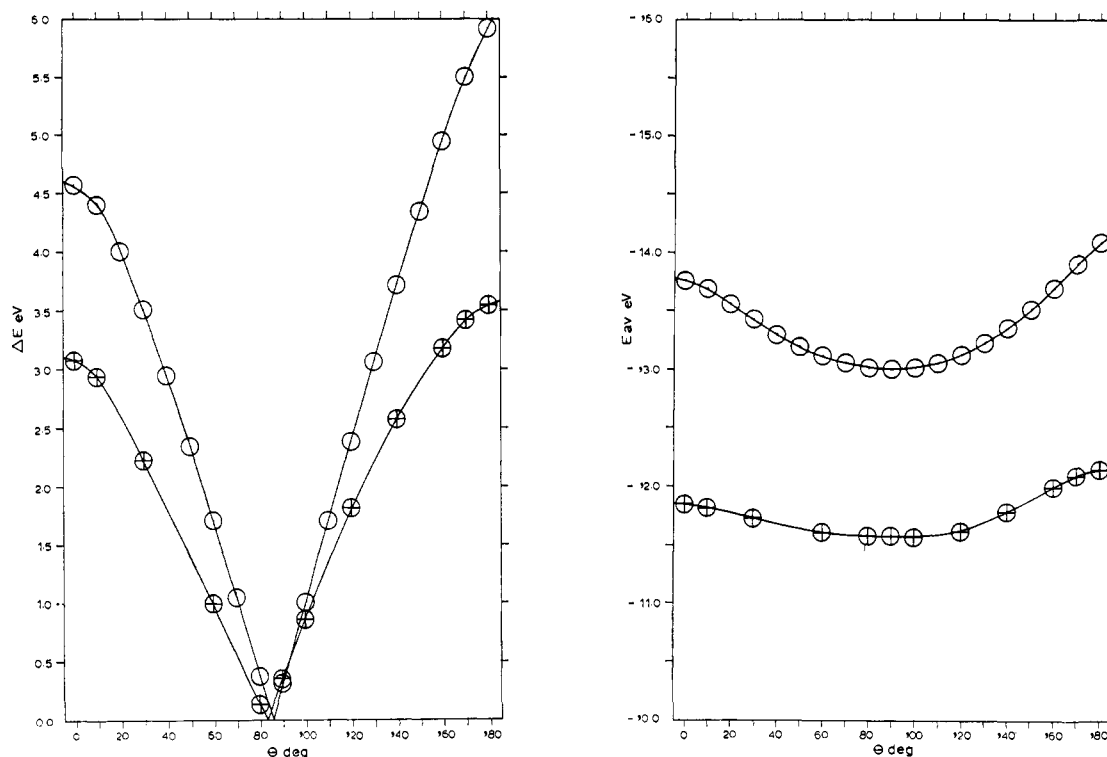
(7) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).

(8) (a) A. Viellard, *Theor. Chim. Acta*, **5**, 413 (1966); (b) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); (c) L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967); (d) H. Yumabe, H. Kato, and T. Yonezawa, *Bull. Soc. Chem. Jap.*, **44**, 22 (1971); (e) E. L. Wagner, *Theor. Chim. Acta*, **23**, 115 (1971).

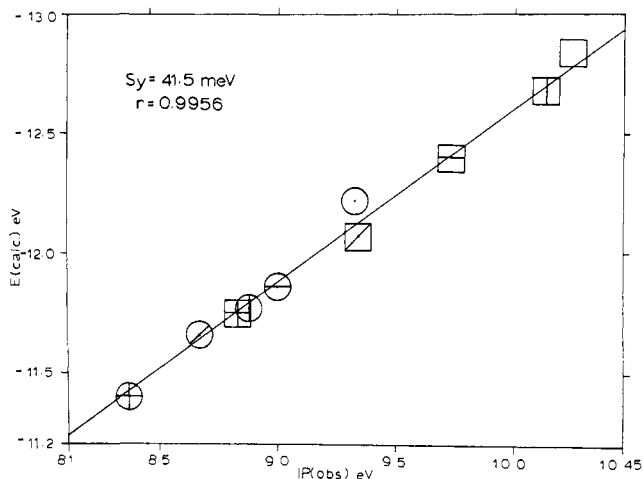
(9) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 2371 (1972).

(10) T. Kasuya, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **56**, 1 (1962).

(11) (a) A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1960); (b) R. P. Lattimer and M. D. Harmony, *J. Chem. Phys.*, **53**, 4575 (1970); (c) *J. Amer. Chem. Soc.*, **94**, 351 (1972).



**Figure 3.** Left: a plot of the difference in energy of the lone pair orbitals *vs.*  $\theta$ : hydrazine (open circles) and tetramethylhydrazine (crossed circles). Right: a plot of the variation of  $E_{av}$  (the averaged energy of the lone pair orbitals) *vs.*  $\theta$ : hydrazine (open circles) and tetramethylhydrazine (crossed circles).



**Figure 4.** Plot of the energy of the lone pair orbitals calculated by INDO,  $\theta = 90^\circ$  ( $E(\text{calcd})$ ), *vs.* the observed ionization potential ( $IP(\text{obsd})$ ) for the methylated hydrazines. Circles are for the highest energy level (first IP), squares for the next (second IP): open figure, methylhydrazine; vertical slash, *uns*-dimethylhydrazine; horizontal slash, *sym*-dimethylhydrazine; diagonal slash, trimethylhydrazine; cross, tetramethylhydrazine.

played graphically in Figure 3. In both cases, the expected<sup>1</sup> orbital crossing occurs near  $90^\circ$ , causing  $\Delta_I$  ( $\Delta_I = E_1 - E_2$ , INDO approximation) to approach zero nearly linearly on either side of the  $\Delta_I = 0$  point as  $\theta$  is changed. Since  $E_{av}$  ( $E_{av} = (E_1 + E_2)/2$ , INDO calculation) is very insensitive to  $\theta$  near  $90^\circ$  (see Figure 3),  $\Delta_I$  is the only useful parameter from the experimental spectra for evaluation of  $\theta$ . Because substitution of methyl for hydrogen has been shown experimentally not to change  $\theta$  very much,<sup>11</sup> we tested whether any of the variation in IP's observed for compounds 2–23 could

be clearly attributed to changes in  $\theta$ , in the following way. The energies for the  $\theta = 90^\circ$  rotamers of the methylated hydrazines, using standard geometries, were calculated by INDO, giving the results of Table II.

**Table II.** INDO Energies for the Lone Pair Orbitals of Methylated Hydrazines,  $\theta = 90^\circ$

Compd	$-E_1$ , eV	$-E_2$ , eV
MeHNNH <sub>2</sub>	12.201	12.840
Me <sub>2</sub> NNH <sub>2</sub>	11.774	12.683
MeHNNHMe	11.861	12.400
Me <sub>2</sub> NNHMe	11.660	12.076
Me <sub>2</sub> NNMe <sub>2</sub>	11.401	11.755

A plot of these INDO energies *vs.* the observed ionization potentials (Table I) gave an excellent straight line, as is shown in Figure 4 and given in eq 1; correlation coefficient ( $r$ ) = 0.9956, standard deviation ( $Sy$ ) =

$$IP_i = (E_i + 5.3734)/(-0.724) \quad (1)$$

42 meV. Since our reproducibility seems to be on the order of  $\pm 30$  meV, there is no evidence from this correlation that  $\theta$  varies significantly for methylated hydrazines. It is difficult to estimate the actual value of  $\theta$  from such a correlation because  $\Delta_I$  is double valued. Thus  $\theta$  could be on the high  $\theta$  branch for hydrazine (as experiment indicates it ought to be, since  $\theta$  values of  $90.2^{10}$  and  $90\text{--}95^\circ$ <sup>11a</sup> have been determined) and on the low  $\theta$  branch of Figure 3 for methylhydrazine (experimentally,  $\theta = 83.3\text{--}84.5^\circ$ <sup>11b,c</sup>; we used the "inner methyl"  $90^\circ$  conformation corresponding to the lowest *ab initio* calculated energy,<sup>11</sup> which also fit our data the best, in Table II and Figure 4). Since there is no reason to believe that the exact  $\theta$  values for crossover of

the lone pair orbitals are given by the INDO approximation, we must ignore this point. We note that both  $IP_1$  and  $IP_2$  values fall near the line of eq 1 (see Figure 4), meaning that both  $IP_{av}$  and  $\Delta$  for the series of methylhydrazines are given to a reasonable accuracy using the INDO approximation and the assumption that  $\theta = 90^\circ$ .

To include the other compounds we ran, we use the fact that there is an essentially perfect correlation between the  $IP_{av}$  values observed for the monoalkylhydrazines 3–8 and  $IP_1$  for the corresponding alcohols.<sup>7</sup> The least-squares line is

$$IP_{av}(\text{hydrazine}) = 0.5658IP_1(\text{alcohol}) + 3.6438 \quad (2)$$

$$(r = 0.9977, \text{ maximum deviation } 14 \text{ meV})$$

We define a parameter  $X_R(\text{hydrazine})$  to quantitatively express the effect of alkyl substitution on the hydrazines, using the above least-squares line effect of eq 2, in eq 3.

$$X_R(\text{hydrazine}) = \frac{IP_{av}(\text{RHNNH}_2, \text{LS})}{IP_{av}(\text{MeHNNH}_2, \text{LS})} \quad (3)$$

Since the effect of changing methyl for another alkyl group causes some changes in the electronic distribution at nitrogen (which is reflected in a decrease in  $IP_{av}$ ), substitution of a second alkyl group for methyl at the same nitrogen ought to cause a slightly smaller effect, because of the presence of the first alkyl group; the effect should not be additive. We follow Fessenden and Schuler<sup>12</sup> (who applied this reasoning to methylated methyl radical central carbon spin densities) and Fischer<sup>13</sup> (who extended it to groups other than methyl) in using a multiplicative relation for such an effect, instead of a strictly additive one. Since  $IP_1$  and  $IP_2$  are equally split about the average IP,  $IP_{av}$ , we can calculate them using  $\Delta_I(\text{LS})$  and  $IP_{av}(\text{LS})$ , the values obtained from the least-squares line of eq 1 (Figure 4), and correcting for the effect of alkyl substitution on  $IP_{av}$  by using eq 4 and 5. Thus  $IP_{av}$  is altered from that for the

$$IP_1(\text{calcd}) = IP_{av}(\text{LS}) \prod_R X_R - \Delta_I(\text{LS})/2 \quad (4)$$

$$IP_2(\text{calcd}) = IP_{av}(\text{LS}) \prod_R X_R + \Delta_I(\text{LS})/2 \quad (5)$$

methylated hydrazine of the proper substitution pattern by multiplying it by the  $X_R$  for each of the alkyl substituents. The values for the necessary parameters for use with eq 4 and 5 are given in Table III.<sup>14</sup> The

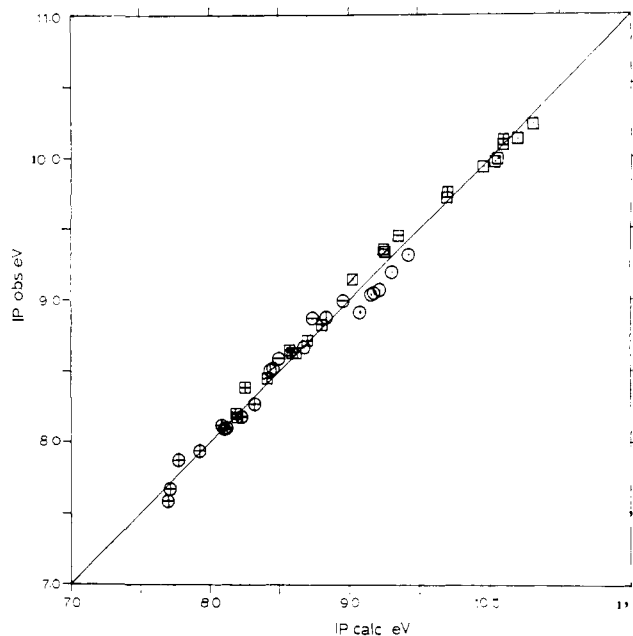
**Table III.** Parameters for Calculation of  $IP_1$  and  $IP_2$  for a Hydrazine Having  $\theta = 90^\circ$  from Eq 4 and 5

Substituent	$X_R(\text{hydrazine})$	Substitution pattern	$IP_{av}(\text{LS})$	$\Delta_I(\text{LS})$
Methyl	1.0	RHNNH <sub>2</sub>	9.872	0.884
Ethyl	0.9884	R <sub>2</sub> NNH <sub>2</sub>	9.468	1.256
<i>n</i> -Propyl	0.9876	RHNNHR	9.332	0.745
<i>i</i> -Propyl	0.9751	R <sub>2</sub> NNHR	8.970	0.575
<i>n</i> -Butyl	0.9722	R <sub>2</sub> NNR <sub>2</sub>	8.570	0.489
<i>tert</i> -Butyl	0.9641			

(12) R. H. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(13) H. Fischer, *Z. Naturforsch.*, **A**, 20, 428 (1965).

(14) As an example, consider 1,1-dimethyl-2-isopropylhydrazine. Since it is a trialkylhydrazine,  $IP_{av}(\text{LS}) = 8.970$ ,  $\Delta_I(\text{LS}) = 0.575$ ,  $X_{Me} = 1.0$ ,  $X_{i-Pr} = 0.9751$  (from Table III). Therefore,  $IP_1(\text{calcd}) = 8.970(1.0)(0.9751) - (0.575)/2 = 8.460$  and  $IP_2(\text{calcd}) = 8.970(1.0)(0.9751) + (0.575)/2 = 9.035$ .



**Figure 5.** Plots of  $IP_1$  (circles) and  $IP_2$  (squares) that were observed by pes vs. the calculated ionization potentials (see text for method). Markings to indicate the alkyl substitution pattern are the same as in Figure 4.

plot of  $IP_i(\text{obsd})$  vs.  $IP_i(\text{calcd})$  is shown in Figure 5, and the least-squares line is given in eq 6. The slope of

$$IP_i(\text{obsd}) = 0.9822IP_i(\text{calcd}) + 0.0158$$

$$r = 0.9942, \text{ Sy} = 78 \text{ meV} \quad (6)$$

about one and intercept nearly zero indicate an extremely good correlation of the observed ionization potentials with a fairly simple calculation, which is based on a constant value of  $\theta$  for all compounds.

From Figure 5, it can be seen that the monoalkylhydrazines 3–8 all deviate approximately uniformly below the least-squares line (eq 6) and that a significant fraction of the observed standard deviation arises from this difference. This may be seen to be a result of the deviation of the MeHNNH<sub>2</sub>  $IP_1$  and  $IP_2$  values from the least-squares line of Figure 4. Since  $\Delta_I$  is adjustable by changing  $\theta$ , we could have improved the fit by choosing a  $\theta$  value different from  $90^\circ$  and moved 3 to 8 closer to the line in Figure 5. We remain unconvinced that the INDO approximation is accurate enough to warrant such "fine tuning" of the  $\theta$  values. Hydrazine and tetramethylhydrazine were calculated to have slightly different  $\theta$  values at  $\Delta = 0$ , and presumably hydrazines of differing substitution might have still different ones. We have no evidence that the calculations actually give correct value of  $\theta$  at  $\Delta = 0$ , although we doubt that the value used is very far off for tetraalkylhydrazines.<sup>15</sup>

In the tetraalkylhydrazine series, where we have nine examples, one might have expected that as larger alkyl groups were substituted the "inner" substituents would interfere with each other enough to force significantly different values of  $\theta$  and cause a change in  $\Delta$ . The only compound for which a hint of such behavior was observed was trisopropylmethylhydrazine (23),

(15) Rademacher's  $\Delta(\theta)$  curve, obtained from MINDO/2 calculations which were rather differently scaled from ours, gives a value of zero for  $\Delta$  at  $\theta = 80.7^\circ$ , only  $2.3^\circ$  different from ours. We thank Professor Rademacher for providing a preprint of this work.

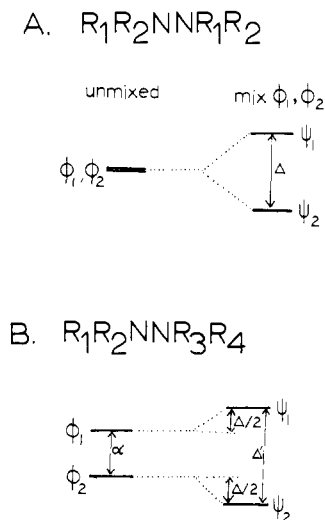


Figure 6. Diagram showing the origin of the "lone pair-lone pair" splittings for symmetrical (A) and unsymmetrical (B) hydrazines.

which had a  $\Delta$  value of 0.61 eV, 80 meV larger than the average of the other eight compounds (this difference in  $\Delta$  is probably significant, though barely so). The slope of the  $\Delta$  vs.  $\theta$  plot for tetramethylhydrazine is 49 meV/deg on the high  $\theta$  branch, and 43 meV/deg on the low  $\theta$  branch, and the plot is linear to  $\pm 30^\circ$  of the crossover point ( $\theta = 83^\circ$ ).<sup>16</sup> Thus, our calculations would indicate that  $\theta$  only deviates by a few degrees from the  $\theta$  values of less hindered hydrazines. It should be admitted that we have ignored the probability of deformations from tetrahedral geometry at nitrogen, which ought to occur to minimize alkyl-alkyl interactions, especially if substantial changes in  $\theta$  do not occur. Such flattening at nitrogen might tend to damp out differences in  $\Delta$  caused by  $\theta$  changes, but the magnitude of such an effect remains to be investigated.

It should be noted that the observed splittings for hydrazine, *sym*-dialkylhydrazine, and tetraalkylhydrazine decrease in that order (0.85, 0.73, and 0.55 eV for the methylated compounds), as do the calculated  $\Delta_T(90^\circ)$  values. For a symmetrical hydrazine, the lone pairs  $\phi_1$  and  $\phi_2$  would have the same energy in the absence of "lone pair-lone pair" mixing (more realistically,  $\phi_1$  and  $\phi_2$  will be mixed with the hydrocarbon substituent orbitals, of course). Interaction of  $\phi_1$  and  $\phi_2$  will produce two MO's  $\psi_1$  and  $\psi_2$  having an energy difference  $\Delta$  (see Figure 6A). If  $\phi_1$  and  $\phi_2$  had decreased electron density at nitrogen (presumably leading to  $\psi_1$  and  $\psi_2$  of similarly reduced density), the value for  $\Delta$  should be less than that for a higher electron density at nitrogen. We suggest that substitution of alkyl for hydrogen does decrease the electron density at nitrogen by greater mixing in of hydrocarbon density in  $\psi_1$  and  $\psi_2$ , leading to the smaller calculated (and observed)  $\Delta$ . This view is supported by the INDO calculations. For  $\theta = 90^\circ$  conformations, the sum of the one-electron AO orbital populations at each nitrogen is 0.43 and 0.41 for  $\psi_1$  and  $\psi_2$  of hydrazine but is decreased to 0.38 and 0.37 in *sym*-dimethylhydrazine and 0.36 and 0.34 in tetramethylhydrazine.

(16) The slopes given refer to the unscaled INDO results and are certainly too large. From consideration of cyclic hydrazines, we prefer a scaling which gives slopes of 31 and 36 meV/deg on the low and high  $\theta$  sides of the crossover point. Justification for the scaling will be given in the near future.

In an unsymmetrical hydrazine,  $\phi_1$  and  $\phi_2$  would have different energies even in the absence of "lone pair-lone pair" interaction; we show this energy difference as  $\alpha$  in Figure 6B. After mixing  $\phi_1$  and  $\phi_2$  to give  $\psi_1$  and  $\psi_2$  the lone pairs will be split by  $\Delta' = \alpha + \Delta$  (Figure 6B). If  $\alpha$  were large compared to  $\Delta$ ,  $\Delta'$  could increase even though  $\Delta$  ought to decrease when compared to a symmetrically substituted hydrazine because of the energy difference between  $\phi_1$  and  $\phi_2$ .<sup>1</sup> We suggest that dominance of the  $\alpha$  term is reflected in the observed  $\Delta$  order for unsymmetrical alkylhydrazines,  $\Delta(\text{MeHNNH}_2) = 0.93 < \Delta(\text{Me}_2\text{NNH}_2) = 1.25 > \Delta(\text{Me}_2\text{NNHMe}) = 0.67$  eV. This is the order expected for the  $\alpha$  terms, since the nitrogens are least similar in the unsymmetrical dimethyl compound.

It will be noted that we did not include an  $\alpha$  term in our consideration of the effect on the pes spectrum for replacement of methyl by a higher alkyl group. The changes in  $\theta$  which could be concealed by a compensating increase in  $\alpha$  and decrease in  $\Delta$  are rather small. For example, if all of the 0.52 eV observed splitting for *uns*-diethyldimethylhydrazine (**16**) were caused by  $\alpha$ ,  $\theta$  must correspond to the value for  $\Delta = 0$  ( $83^\circ$  in our INDO approximation). The constancy in observed splittings for **15**–**17** makes it appear that there is not a detectable  $\alpha$  value induced by replacement of two methyls by ethyls.

We will turn to the problem of using pes to evaluate conformation of cyclic hydrazines, where changes in  $\theta$  obviously occur,<sup>2,3</sup> as well as of other systems, in future publications.

## Experimental Section

**Compounds.** Commercial samples of **2**,<sup>17</sup> **3**, **9**, and **11** were employed. Monoalkylhydrazines **4**–**8** were prepared by alkylation of hydrazine hydrate<sup>18</sup> and isolated by distillation. 1,1-Di-*n*-propylhydrazine (**10**) was prepared by zinc amalgam reduction of the *N*-nitroso compound<sup>19</sup> and 1,2-di-isopropylhydrazine (**12**) by reduction of acetone azide.<sup>20</sup> Tri- and tetramethylhydrazine (**13**, **15**) were prepared by reduction of the related formates.<sup>21</sup> 1,1-Dimethyl-2-isopropylhydrazine was prepared by sodium borohydride reduction<sup>22</sup> of the acetone hydrazone of 1,1-dimethylhydrazine and isolated by distillation, bp (atm) 82–84°. Compounds **17**–**23** were prepared by reductive alkylations using sodium cyanoborohydride.<sup>23</sup> The preparations of **16** and **19** have been described elsewhere.<sup>24</sup> All compounds had the expected boiling points and nmr spectra. All were purified before use by vpc (Varian Aerograph 90-P, 10 ft  $\times$  0.25 in. 15% XF, 1150 on 60–80 mesh Chromosorb W column).

**INDO Calculations.** We used Pople's INDO program<sup>25</sup> and "standard geometry" as used by Pople:<sup>25b</sup>  $R(\text{C}-\text{C}) = 1.54$ ,  $R(\text{N}-\text{N}) = 1.45$ ,  $R(\text{C}-\text{N}) = 1.47$ ,  $R(\text{C}-\text{H}) = 1.09$ ,  $R(\text{N}-\text{H}) = 1.01^\circ$ , all bond angles tetrahedral ( $109.47^\circ$ ), and dihedral angles defined by using staggered conformations for bonds connecting atoms with tetrahedral angles.

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**Pes Spectra.** A Varian IEE-15 spectrometer adapted for uv work was employed. Unpolarized He 584-Å light was used for sample irradiation. Ionization potentials were measured relative to the Ar 15.759-eV line, and typical spectra were time averaged over 40 30-sec scans. All compounds were freshly purified by vpc before determination of the pes spectrum, and all spectra reported here were obtained at ambient temperature.

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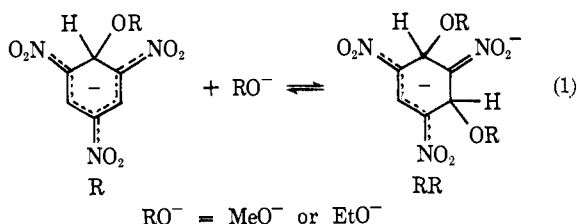
## Normal Coordinate Analysis of Coupled Reactions. Application to Anionic $\sigma$ Complexes of 1,3,5-Trinitrobenzene with Hydroxide and Alkoxide Ions in Water, Methanol- Water, and Ethanol-Water Mixtures<sup>1</sup>

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**Abstract:** The kinetics of 1:2 complex formation between 1,3,5-trinitrobenzene (TNB) and the three nucleophiles  $\text{HO}^-$ ,  $\text{MeO}^-$ , and  $\text{EtO}^-$  have been measured by the stopped-flow technique. In the mixed solvents the competition between  $\text{RO}^-$  and  $\text{HO}^-$  results in the formation of three different 1:2 complexes ( $\text{TNB}\cdot 2\text{RO}^-$ ,  $\text{TNB}\cdot 2\text{HO}^-$ ,  $\text{TNB}\cdot (\text{RO}^-)(\text{HO}^-)$ ). This should give rise to three chemical relaxation processes, but only two such processes could be observed. By applying the principles of normal coordinates to chemical reactions, it can be shown that in the not unlikely event where two of the complexes ( $\text{TNB}\cdot 2\text{RO}^-$  and  $\text{TNB}\cdot (\text{RO}^-)(\text{HO}^-)$ ) dissociate with similar rates, one of the relaxation processes must indeed escape detection. A similar normal coordinate analysis demonstrates further that the reason why no cis-trans isomerism is observed in the 1:2 complexes may be an equality or similarity of rates of dissociation for the cis and trans isomer. A physical interpretation of the conclusions reached on the basis of mathematical relationships is offered.

Diadducts formed by the attack of a second molecule of nucleophile on Meisenheimer complexes have been reported in several systems.<sup>3</sup> If the nucleophile is an anion, the diadduct or 1:2 complex bears at least two negative charges which makes water a particularly favorable medium for its formation.<sup>4</sup> Thus, we expected that reactions such as eq 1 would proceed



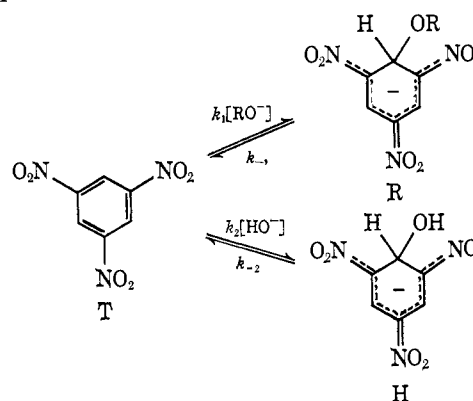
more easily to the right in alcohol-water mixtures of high-water content than in the respective pure alcohols.

In a previous paper we reported the kinetics of the 1:1 complex formation between 1,3,5-trinitrobenzene (TNB) and the bases  $\text{HO}^-$  and  $\text{MeO}^-$  or  $\text{EtO}^-$  in 22.5%  $\text{MeOH}$ -77.5%  $\text{H}_2\text{O}$  (v/v) or in 19%  $\text{EtOH}$ -81%  $\text{H}_2\text{O}$  (v/v), respectively.<sup>5</sup> It was mentioned that basic

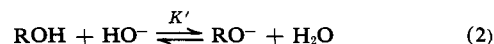
solutions of TNB in these solvent mixtures are characterized by a total of four relaxation processes.

The two shortest relaxation times,  $\tau_1$  and  $\tau_2$ , in a given solvent mixture arise from the reactions of Scheme I, where it is understood that the two com-

Scheme I



peting nucleophiles are in a mobile equilibrium according to eq 2. In both solvents the reaction with



$\text{RO}^-$  is responsible for the shortest relaxation time ( $\tau_1$ ).

In this paper we show that the third and fourth relaxation times,  $\tau_3$  and  $\tau_4$ , are associated with the attack of a second molecule of base on R and H, respectively, to form the 1:2 complexes RR (eq 1), HH, and RH. This is shown in Scheme II.

(1) This is part XIII in the series "Intermediates in Nucleophilic Aromatic Substitution." Part XII: C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, **39**, 1054 (1974).

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