vacuum oven at 100–110 °C overnight.

Method B. The same O-alkylation procedure may be employed with a 25% solution of tetrabutylammonium hydroxide. Two modifications are required in the previous experiment if this base is used. First, the reaction time is less than 1 day, and second, during the workup sodium nitrate (3-fold excess) is added just after neutralization to produce an anion-exchange reaction with the tetrabutylammonium salt. Since the quaternary ammonium nitrate is more water soluble than the corresponding halide derivative, the sodium nitrate addition lessens the time required to wash out the tetrabutylammonium byproduct. The sodium salts were readily removed by the hot water extractions. The Soxhlet extraction time is about the same with this modified procedure as before.

Method C. Octadecylation Reaction. The octadecylation of a coal requires a special workup as well as twice the reaction time as the general procedure already described. For removal of excess octadecyl bromide, methanol was used instead of water throughout the entire procedure. Methanol is an excellent solvent for tetrabutylammonium halides. Fortunately, O-octadecylated coal is virtually insoluble in methanol. Thus, all the reagents can be easily removed from the alkylated coal product.

II. Rawhide Coal. The same general procedure used for Illinois no. 6 coal works equally well for Rawhide with some modifications.

Method A. Rawhide coal (50.00 g of −80 U.S. mesh, or 250 mmol of active sites) was placed in a 2-L, round-bottomed flask under a nitrogen atmosphere. Tetra-*n*-butylammonium hydroxide (1.00 M in water, 260 mL, 260.0 mmol, or a slight excess over the available acidic protons) was charged into the flask. Tetrahydrofuran (500 mL) which was freshly distilled from lithium aluminium hydride was also added. Finally, iodomethane (198.26 g, 1396.79 mmol) was added with vigorous mixing to the reaction vessel. The reaction was complete in a few hours, but it was allowed to stir overnight. The workup is the same as that used for the Illinois no. 6 coal.

Note: In O-alkylation of coals only a slight excess of base is used. The use of a 2-fold excess does not have any appreciable effect on the rate of alkylation. It serves only to complicate the workup because it becomes necessary to wash out the additional quaternary salts from the product. There is also a competing side reaction in the presence of excess base, a slow hydrolysis of the alkylating reagent to produce an alcohol which in a subsequent step undergoes O-alkylation to produce an ether. Obviously, this ether would have to be removed from the coal product. This would be most troublesome for the larger alkylating reagents since the ether produced from a C_1 to C_4 alkylating agent is easily distilled out of the product during normal workup conditions. Fortunately, this hydrolysis alkylation is relatively very slow and was not a problem in the course of this study except for the O-benzylation reaction since benzyl bromide hydrolyzes more readily than normal alkyl halides. Therefore, in this case the benzyl bromide was added dropwise to the stirred reaction mixture, and only a slight excess of alkylating agent was used in order to minimize the competing side reaction. Methanol was used during the workup instead of water.

Acknowledgment. The authors gratefully acknowledge many valuable discussions with Drs. P. H. Given, M. L. Gorbaty, and J. W. Larsen. We are indebted to Messers G. B. Brons, H. J. Malone, and R. A. Salher for their experimental expertise.

Supplementary Material Available: Infrared spectra of Illinois No. 6 coal, Rawhide coal, and alkylated derivatives thereof; ^{13}C NMR spectra of methoxyl derivatives of the above two coals (8 pages). Ordering information is given on any current masthead page.

Effects of Structure on the Ease of Electron Removal from *o*-Phenylenediamines. 2. Photoelectron Spectra of *o*-Phenylenediamines

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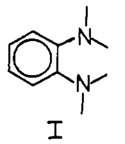
Photoelectron spectra are reported for *o*-phenylenediamine and 14 acyclic and N,N′-monocyclic alkylated derivatives, as well as for 2,3-benzo-1,4-diazabicyclo[2.2.2]oct-2-ene (**14**) and its 3′,6′- and 4′,5′-dimethyl derivatives and 9,10-benzo-1,5-diazabicyclo[3.3.2]dec-9-ene (**15**). Photoelectron spectroscopy does not appear to be useful for the determination of conformations in these compounds because of the strong interaction between the effects of bending and twisting at nitrogen on ionization potentials. Comparison of photoelectron and cyclic voltammetry data leads to estimates of 5.3 and 14.1 kcal/mol, respectively, for the destabilization of *N,N,N′,N′*-tetramethyl-*o*-phenylenediazine radical cation and $15^{+\cdot}$ relative to an unstrained, planar tetraalkyl-*o*-phenylenediamine radical cation.



I

We previously reported a cyclic voltammetry (CV) study of several *o*-phenylenediamine derivatives (I) in butyronitrile solution.[1] In most cases formal potentials for reversible electron transfer (here called $E^{\circ\prime}$) were measured for removal of both the first and second electron from I. Values of $E^{\circ\prime}$ (I, $I^{+\cdot}$) were observed to vary over a range of 1.1 V, corresponding to a ΔG° range of 25 kcal/mol. We report here photoelectron spectroscopy (PES) measurements on the same compounds. PES measurements provide vertical, vapor phase, I,$I^{+\cdot}$ energy differences, which make an interesting comparison with the adiabatic, solution values provided by the CV work. PES measurements have proven useful in determining the amount of rotation about the NN bond of hydrazines,[2,3] and we wished to

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(1) Nelsen, S. F.; Clennan, E. L.; Echegoyan, L.; Grezzo, L. A. *J. Org. Chem.* **1978**, *43*, 2621.

(2) (a) Rademacher, P. *Angew. Chem.* **1973**, *85*, 410. (b) Rademacher, P. *Tetrahedron Lett.* **1974**, 83. (c) Rademacher, P. *Chem. Ber.* **1975**, *108*, 1548. (d) Rademacher, P.; Koopman, H. *Ibid.* **1975**, 1088, 1557.

0022-3263/81/1946-0283$01.00/0

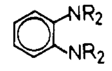
Table I. Photoelectron Spectra of some *o*-Phenylenediamine Derivatives

compd	IP_1	IP_2	IP_3	IP_4
4-H	7.73	8.63	10.69	11.12
4-Me	7.36	8.06	9.28	9.70
4A-Me	7.66	8.42	(8.94)	
4B-Me	7.07	7.84	(9.08)	
5-Me	7.06	8.29	9.89	10.26
6-H	7.16	8.19	10.06	10.42
6A-H	6.95	7.75	9.76	10.02
6B-H	6.88	7.90	9.82	10.17
6-Me	6.85	7.96	9.62	9.97
6A-Me	7.42	7.78	8.68	9.56
6B-Me	5.65	7.69	9.26	9.65
7-Me	7.27	8.27	9.18	9.61
8-Me	6.86	7.85	9.28	9.87
9-Me	7.08	7.95	(9.34)	
12-Me	6.60	7.92	9.52	9.90
15	7.91	8.26	8.77	9.08

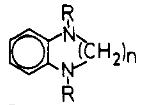
evaluate the utility of photoelectron spectroscopy for the determination of I conformations. This would be particularly valuable for I, because the low nitrogen inversion barriers prevented NMR from giving significant conformational information for these compounds.[1] The PES time scale is extremely short, allowing observation of the superposition of photoelectron spectra for the conformations present,[2,3] instead of time-averaged values as are seen in NMR. Another reason for wanting PES data for I was to determine the first vertical ionization potentials, IP_1, to allow separation of the effect of the energy of the highest occupied molecular orbital (HOMO) on the $E°'$ values. This information has proven useful in analogous studies of hydrazines and 2-tetrazenes.[4]

Results

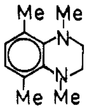
Photoelectron Spectroscopy. The PES data for the compounds studied are summarized in Table I (the BenzoDabco derivatives **14**, **14A**, and **14B** will be considered separately, below). For convenience, the compound numbering employed is the same as in the previous paper:[1] **4-R**



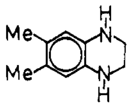
4-H R=H
4-Me R=Me



5-Me n=1,R=Me
6-H n=2,R=H

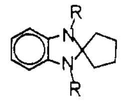


6A-Me

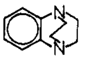


6B-H

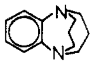
is used for compounds in which the nitrogens are not linked, **5-R** to **9-R** are used for the five- to nine-membered heterocyclic ring examples in which the link connecting the nitrogen is a $(CH_2)_n$ bridge, and R indicates the other substituents on nitrogen. Once again, suffix A is employed for 3,6-dimethyl and B for 4,5-dimethyl ring-substituted compounds. Other compounds studied include the spiroalkyl five-membered heterocyclic ring compound **12-Me** and the benzobicyclic examples **14** and **15**.



12-Me R=Me



14



15

The photoelectron spectra are complex and show partially overlapping peaks in the low-IP region (see Figure 1 for examples). All of the IP values reported in Table I are positions obtained with a four-peak, Gaussian, least-squares fit to the experimental data in the low-IP region where four peaks are expected.

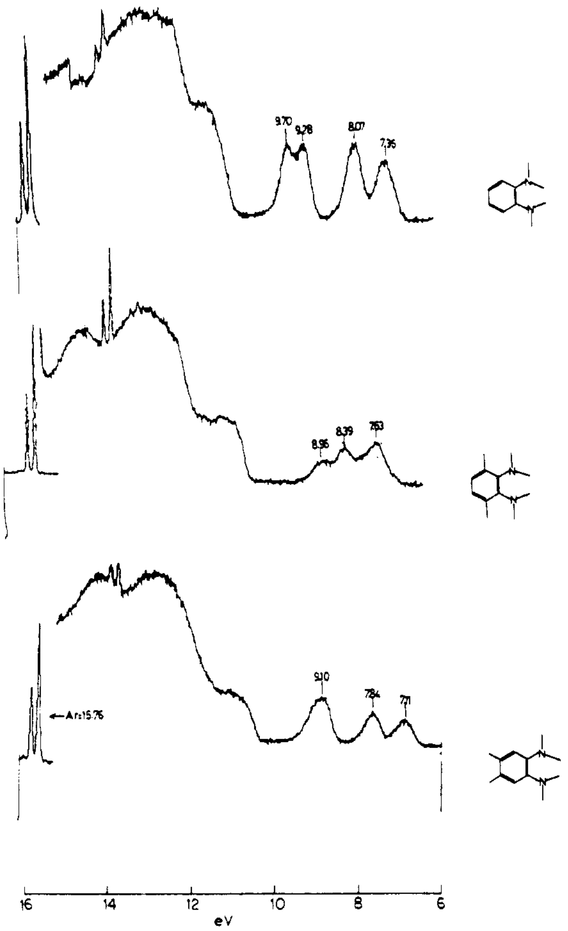
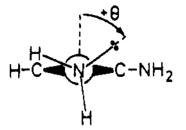
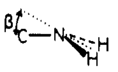


Figure 1. Photoelectron spectra of compounds **4-Me**, **4A-Me**, and **4B-Me**.

MINDO/3 Calculations on 4-H. For assignment of the photoelectron spectra, semiempirical MO calculations were performed on *o*-phenylenediamine (**4-H**) by using the MINDO/3 method.[5] We were particularly interested in finding out how the orbital energies are predicted to vary with geometry at nitrogen, because the geometries at nitrogen must be varying considerably among the compounds studied. We shall discuss the geometry at nitrogen in terms of the CN rotational angle θ (defined as 0° when the N lone-pair orbital axis is coplanar with the ring carbon p orbital axis; see II) and the angle of bending at nitrogen



II



III

(β, the angle the CN bond makes with the HNH plane; see III). Because 54 geometrical parameters would need to be varied for true minimization of the energy of **4-H**, we employed several simplifying assumptions to make our calculations feasible. C_2 symmetry was enforced, all atoms except the NH hydrogens were held coplanar, the four CH bond lengths were forced to be the same, as were the four NH bond lengths, and the HCC bond angles nearest the ring nitrogens were fixed at 120°. With these assumptions,

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[3] Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6982, 6987 and references therein.

[4] (a) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269. (b) Nelsen, S. F.; Peacock, V. E. *Ibid.* **1977**, *99*, 8354. (c) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978**, *100*, 7017.

[5] Dewar, M. J. S.; Bingham, R. C.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1284, 1294, 1302.

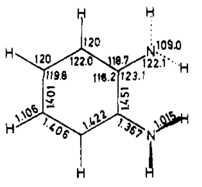

Figure 2. MINDO/3 geometry calculated for 4-H in the $\theta = 0°$ conformation by using the assumptions listed in the text.

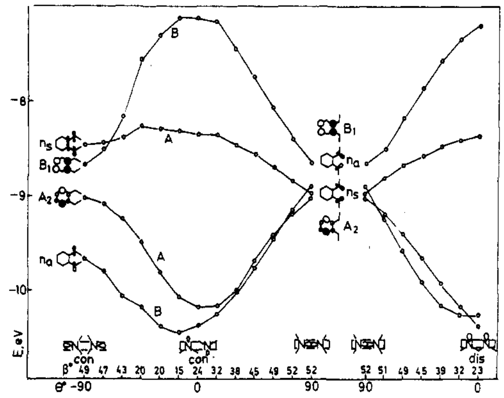

Figure 3. Plot of the four highest occupied orbital energies (MINDO/3) as a function of θ and the values of β calculated at each θ for C_2 conformations.

it was still necessary to vary 11 geometrical parameters to minimize the MINDO/3 energy for the $\theta = 0°$ (con) conformation, giving the geometry shown in Figure 2. MINDO/3 attributes quinoid character to the benzene ring, as might be expected for $\theta = 0°$. The structure obtained has the usual shortcomings of the MINDO/3 method, with the CN bonds undoubtably too short and the CC bond lengths too long, as expected from published MINDO/3 studies of aniline and toluene.[5] The NH_2 groups are calculated to be nonplanar, with $\beta = 24°$. We then performed CN twisting calculations in 15° increments from the $\theta = 0°$ (con) to $\theta = -90°$ (con); the CN has lone pairs coplanar with the benzene ring and directed toward each other. Another set was performed from $\theta = +90°$, with disrotatory twisting to the $\theta = 0°$ (dis) conformation, with the lone pairs parallel and both on the same side of the benzene ring (see Figure 3 for end-on views of these conformations). To keep these calculations feasible, we fixed the aromatic ring parameters at the $\theta = 0°$ (con) values (Figure 2), while the geometry at the nitrogens was allowed to relax (CN and NH bond lengths; CCN, CNH, and HNH bond angles) at each θ value. A plot of the orbital energies thus calculated for the four highest MO's as a function of θ is shown in Figure 3, along with the energy-minimized β values obtained. Many geometrical assumptions are involved in these calculations, but it is clear that β is predicted to be small when there is large lone pair–aryl π electron interaction (θ near 0°) and to approach a tetrahedral value (54.7°) when θ is near ±90°. The minimum value of β of 15° was calculated near $\theta = -15°$ (dis), presumably to reduce NH,NH interaction, as does the slightly smaller β at -90° than that at +90°. The many geometrical assumptions make $\Delta H_f°$ values thus calculated of little significance even for the MINDO/3 approximation, but a minimum total energy was attained at $\theta \approx +15°$ (con), 3.9 kcal/mol more stable than at $\theta = +90°$ (con) and 6.0 kcal/mol more stable than at -90° (con). The calculations indicate quite shallow energy curves for changing β at a given θ, as expected. For $\theta = 0°$ (con), bending to $\beta = 50°$ caused a 2.30-kcal/mol increase in $\Delta H_f°$, and flattening at 0° only increased $\Delta H_f°$ 0.13 kcal/mol. Sets of varied θ calculations were also performed between θ (con) = -90° and $\theta = +90°$ at fixed β values of 20° and 50° to see how β changes affect the orbital energies calculated at a given θ. There are significant effects on the orbital energies, but the ordering of the first four MO's is not affected between $\theta = -60°$ and +60°. These calculations suggest that the first two orbitals for compounds with significant lone pair–aryl π interaction may be assigned confidently in the order B, A, although the assignment of the closely spaced third and fourth IP's is uncertain, as indicated in Figure 3. The separation between the orbitals is sensitive both to β and θ, as is indicated in Figure 4, which includes points for the variable β, $\beta = 20°$, and $\beta = 50°$ conrotatory twist calculations. Nevertheless, the ratio of $(E_1 - E_2)/(E_3 - E_2)$ is calculated to be nearly constant (0.61–0.70) when θ is between −30 and +30° for all twisting calculations. Therefore, PES peak separations are not predicted to be useful for distinguishing β and θ effects; they are quite thoroughly coupled.

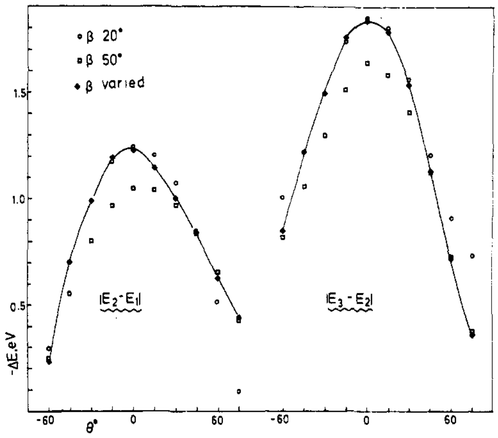

Figure 4. Plot of the MINDO/3 energy separation between the two highest occupied MO's of 4-H ($|E_2 - E_1|$) and between the next two orbitals ($|E_3 - E_2|$) as a function of θ for C_2 conformations.

Discussion

Effects of the Degree of Bending at Amino Nitrogen on Photoelectron Spectra. A principal problem in deriving conformational information from PES data for I derivatives is the fact that these data are very sensitive not only to the degree of lone-pair aryl interaction and the size of the attached alkyl substituents but also to the amount of bending at nitrogen (and hence lone-pair hybrization). A study of 9-alkyl-9-azabicyclo[3.3.1]nonane photoelectron spectra indicated that the 9-*tert*-butyl compound shows an IP_1 value 0.3 eV lower than it would have if the nitrogen had not flattened due to increased steric interactions.[6] Although β is convenient to use to define bending at nitrogen in calculations, semiempirical MO calculations predict that the change in IP_1 is nearly linear with the fraction of p character in the lone-pair hybrid, and a plot of calculated IP vs. β is very nonlinear (see ref 6, Figure 2), although it is much more nearly linear with changes in α_{av}, the average of the three RNR′ angles about the nitrogen. The major change in IP_1 occurs in the first stages of flattening (using β as the angle discussed), and the PES data for the 9-*tert*-butyl compound mentioned above were consistent with a β angle as large as 45°.

The considerable sensitivity of even hydrazine photoelectron spectra to the rehybridization effects associated with flattening at nitrogen has not been summarized succinctly before, and we take the opportunity to do so

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[6] Nelsen, S. F.; Kessel, C. R.; Brien, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 702.

here. Surprisingly, hexahydropyridazine (1,2-diazacyclohexane) derivatives which have two occupied conformations, diequatorial (lone pairs anti, lone pair–lone pair dihedral angle $\theta' = 180°$, $IP_2 - IP_1 = 2.3$ eV) and axial equatorial (lone pairs gauche, $\theta \approx 70°$, $IP_2 - IP_1 = 1.0$ eV), accidentally show the same IP_1 values for both conformations.[2,3] This requires that the average of the lone-pair ionizations for the diequatorial conformation be significantly higher than that for the axial–equatorial conformation (by 0.61 eV, using the most recent PES data available).[7] This anomalous difference in average ionization potentials caused Cowley and co-workers to question the above assignment,[8] but we believe that more recent X-ray structure determinations[9] have shown how the anomaly arises. The nitrogens of anti, lone-pair, six-ring tetraalkylhydrazines prove to be significantly more bent ($f_p = 0.69$–0.72, $\alpha_{av} = 107.4$–$108.3°$, $\beta_{av} = 57.6$–$59.6°$) than those of a gauche lone pair compound ($f_p = 0.79$–0.82, $\alpha_{av} = 110.9$–$112.2°$, $\beta_{av} = 47.4$–$51.0°$). The higher f_p gauche conformation should indeed show a lower IP_{av}, and we believe the overlap of the IP_1 values for the gauche and anti lone-pair hydrazines is caused by the rehybridization at nitrogen.

The coupling of twisting and bending will be much more important in aniline derivatives, where nitrogen bending barriers are far lower than those in hydrazines. While hydrazines show fairly small bending changes upon NN bond rotation (f_p increases about 0.1, α_{av} increases about 3°, and β_{av} decreases about 11° in going from anti to gauche lone-pair hydrazines), the structural changes in the I derivatives studied are much larger. The nitrogens probably vary from nearly planar, as in the $\theta \approx 0°$ compound **12**-Me (see below) to nearly tetrahedral in the $\theta = -90°$ compound **14**, corresponding to an f_p decrease of 0.25, an α_{av} decrease of 10.5°, and a β_{av} increase of 54.5°. When this is coupled with the apparent sensitivity of IP to alkyl group configuration revealed in other hydrazine work[4c] and the great coupling of β and θ effects emphasized in Figure 4, it appears unreasonable to expect that PES data will be very useful in determining either β or θ for an intermediate aryl π electron–lone pair interaction case like **6**-Me or **7**-Me. We must admit defeat in being able to use photoelectron spectroscopy to determine conformations of I.

Photoelectron Spectra of I Derivatives. Comparison of the IP's observed for **12**-Me and **5**-Me illustrates the importance of β in determining lone pair–aryl π electron interaction. Although the atoms of the heterocyclic ring are probably almost planar for both, the nitrogens of **5**-Me are expected to be somewhat bent on electronic (from the MINDO/3 calculations on **4**-H and the known structure of aniline) and steric (reducing NCH_3, aryl-ring interaction) grounds. This bending at N will make θ some small, possibly negative (con), number, although if the CH_2 were bent significantly out of the aryl-ring plane, a positive θ (dis) would presumably result. For **12**-Me, bending at N will increase NCH_3–spiro ring steric interaction, so β and hence θ should be smaller. Experimentally, $\Delta_{12} = IP_2 - IP_1$ is 0.09 eV smaller for the more bent **5**-Me.

Figure 5 is a pictorial display of the first four IP values for **5**-Me to **9**-Me as well as the tetramethyl compound **4**-Me and the $\theta = -90°$ (con) compound **15**. The IP's are seen not to have a very regular distribution with heterocyclic ring size, although Δ_{12} does decrease in the order **5**-Me > **6**-Me > **7**-Me ≈ **8**-Me > **9**-Me > **4**-Me > **15**. The higher IP's for **5**-Me than other compounds presumably include an inductive effect; the nitrogens of **5**-Me are CH_2N substituted instead of CH_2C substituted as for the other compounds. As shown diagramatically in the end-on views, **6**-Me and **7**-Me should have larger θ values than

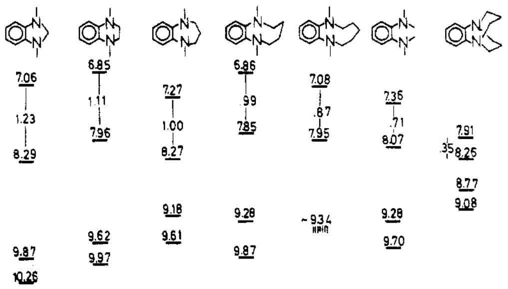
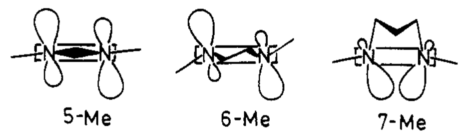
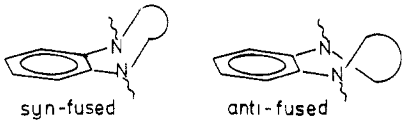


Figure 5. Comparison of the first four IP's for **4**, **5**-Me, **6**-Me, **7**-Me, **8**-Me, **9**-Me, **4**-Me, and **15**.



5-Me, and the electronic tendency to increase β at larger $|\theta|$ would only tend to increase the difference in lone pair–aryl π electron interaction. Pseudoequatorial *N*-methyl groups were drawn in the diagrams, but our only experimental evidence either that this is the case or that any one conformation predominates is that when 3,6-methyl groups are present in **6A**-Me, Δ_{12} is greatly decreased (to 0.36 eV). The presence of *o*-methyl groups will surely destabilize the bis(pseudoequatorial *N*-methyl) conformation, and a large effect is seen on the photoelectron spectrum. The reason for a 0.41-eV decrease in IP_1 between **7**-Me and **8**-Me with no change in Δ_{12} is not clear, although a syn-fused **7**-Me would have the *N*-methyl groups nearly coplanar with the ring and might not have both *N*-methyl groups pseudoequatorial. When enough methylenes span the two nitrogens, one would expect anti-fused conformations to be favored. The substantial similarity of the photoelectron spectra of **9**-Me and **4**-Me suggests to us that **9**-Me may well be anti fused, but the problem of not being able to specify the stereochemistry of the *N*-methyl groups prevents accurate conformational analysis of these compounds. About all one can really conclude is that θ for **9**-Me and **4**-Me is larger than for **7**-Me and **8**-Me.



The increased IP_1 and small $IP_1 - IP_4$ spacing of **15** are consistent with the MINDO/3 calculations for **4**-H with $\theta = -90°$ (con), the conformation at nitrogen enforced by the two methylene chains bridging the nitrogens.

Photoelectron Spectra of BenzoDabco Derivatives. The photoelectron spectra for **14** and its dimethyl derivatives are considerably different from those of **15**, although all are held in $\theta = 90°$ (con) conformations. This is expected because of the large through-bond interaction known to occur in 1,4-diazabicyclooctane (Dabco) itself, where PES studies have shown that the highest occupied

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[7] Schweig, A.; Thon, N.; Nelsen, S. F.; Grezzo, L. A. *J. Am. Chem. Soc.*, in press.

[8] Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Padolina, M. *J. Am. Chem. Soc.* **1974**, *96*, 2648, footnote 7. The assignments made here by Cowley and co-workers for diphosphine derivatives have been shown to be incorrect: Schweig, A.; Thon, N.; Vermeer, H. *Ibid.* **1979**, *101*, 80.

[9] (a) Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461. (b) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *Ibid.* **1978**, *100*, 7876.

Table II. ^{13}C NMR Shifts of *o*-Phenylenediamine Derivatives

compd	solvent[a]	C_{11}	C_{36}	C_{45}	others
4-H	C	134.76	116.79	120.24	
4B-H	C	132.42	118.61	127.83	18.84
4-Me	C	144.73	118.09	121.90	41.63
4-Me	A	145.78	118.33	122.31	41.54
4B-Me	A	143.75	120.04	129.38	41.99, 19.11
5-Me	C	143.12	105.97	119.05	80.19, 34.29
12-Me	C	140.72	102.80	117.65	97.7, 31.80, 28.54, 26.17
12B-Me	C	139.18	105.50	124.22	97.88, 31.08, 28.19, 26.11, 19.43
6-H	C	133.71	114.72	118.70	41.46
6B-H	C	131.56	116.65	126.48	41.96, 18.83
6-Me	C	136.25	110.28	117.73	49.80, 39.08
6B-Me	C	135.02	113.14	125.35	50.33, 39.50, 19.06
7-H	C	140.56	119.91[b]	120.96[b]	47.31, 32.63
7-Me	C	143.17	117.10[b]	121.29[b]	53.60, 42.30, 26.56
8-H	C	141.00	121.92[c]	121.92[c]	48.47, 28.54
8-Me	C	142.60	115.66[b]	119.63[b]	51.23, 38.17, 25.78
9-Me	C	144.80	116.60[b]	120.57[b]	53.28, 37.21, 26.89, 28.77
15	A	152.47	128.05[b]	129.05[b]	51.38, 29.06

[a] C is $CDCl_3$, and A is $(CD_3)_2CO$. [b] $C_{4,5}$ methylation data not available; assignment uncertain. [c] Only one peak for C_{36} and C_{45} at 25 MHz; 0.04 ppm separation seen at 50.1 MHz.

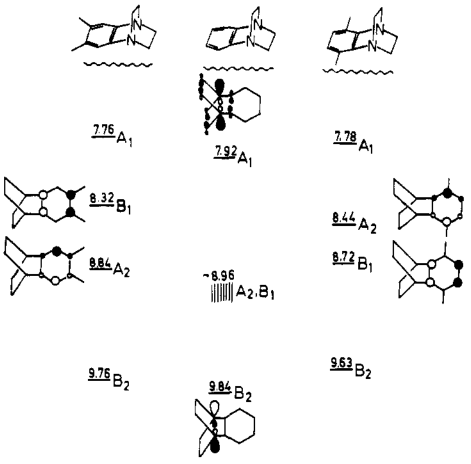

Figure 6. Comparison of $IP_1 - IP_4$ for 14, 14A, and 14B, with assignments based on a MINDO/3 calculation for 14.

orbital is the A_1' orbital resulting from lone pair–σ(C–C) interactions,[10] as predicted by Hoffmann and co-workers.[11] The observed vertical ionization potentials for 14, 14A, and 14B are shown in Figure 6. All showed distinct structure in the first ionization band: for 14, a separation averaging 0.09 eV was observed for six distinct maxima, and IP_a = 7.64 for the first-observed fine-structure maximum (fofsm); for 14A, an average separation of 0.09 eV was observed for four distinct maxima, and IP_a = 7.50 for the fofsm; for 14B a 0.08_5 average separation was observed, and IP_a = 7.49 for the fofsm. These vibrational splittings are close to those found for Dabco, about 0.10 eV.[10b] A MINDO/3 calculation on idealized[12] 14 gave orbitals at −7.77 (A_1), −8.63 (B_1), −9.05 (A_2), and −9.47 (B_2) eV; IP_1 at 7.92 eV is 0.15 eV more stabilized than the calculated value (assuming Koopmans theorem). We failed to resolve distinct bands for the second two ionizations of 14, calculated to differ in energy by 0.43 eV, and the fourth PES peak is stabilized by 0.37 eV compared to the calculation for the B_2 orbital. Each IP is lower for 14A and 14B than for 14, as expected from the methyl substitution. Both show clear resolution of B_1 and A_2 ionization peaks. The assignments of Figure 6 (B_1 is 0.52 eV more stabilized relative to A_2 for 14B but A_2 is 0.28 eV more stabilized relative to B_1 and 14A) are those expected by assuming a larger destabilization for an orbital with a larger p coefficient at the position of methyl substitution. These assignments are consistent with the literature assignments for *p*-xylene [8.17 (A) and 9.2 (S) eV][13] and *o*-xylene [8.75 (S) and 9.10 (A) eV].[14]

13C NMR and Lone Pair–Aryl Ring Interaction. Carbon-13 NMR para shifts are known to correlate well with measures of aryl ring electron density such as Hammett σ values.[15] Thus the remote carbon (C_{45}) shifts of I derivatives ought to provide another spectroscopic measure of lone pair–aryl ring interaction. The shifts we previously reported[1] were largely misassigned between C_{36} and C_{45}, but the proper assignments are now clear from the shifts observed upon methylation at C_{45}. For systems 4-H, 4-Me, 6-H, 6-Me, 12, and 14, methylation at C_{45} causes larger downfield shifts at C_{45} (6.6–7.8 ppm) than at C_{36} (0.9–2.9 ppm), and these shifts are comparable to those observed for similar methyl substitutions on benzene, toluene, and xylene.[16] The corrected ^{13}C NMR shifts for I derivatives appear as Table II. Where C_{45}-methylated compounds are not available, we have tentatively made the assignment of the downfield aryl CH peak to C_{45}, which is true for all the verified cases, but this is obviously tentative for 7-H and 15, where C_{36} and C_{45} only differ by about 1 ppm; for 8-H, these carbons only differ in shift by 0.04 ppm.

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[10] (a) Bischiff, P. A.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedron Lett.* **1969**, 4025. (b) Heilbronner, E.; Muszkat, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 3818. (c) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1974**, *96*, 7930.

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[12] C_{2v} symmetry was enforced, with a planar benzene ring having all CCC and CCH bond angles of 120°. The local symmetry of the bicyclo[2.2.2]octyl system heavy atoms was C_{3v} (i.e., all three CNC bond angles in a Newman projection along the NN axis were 120°). The four aryl CH bond lengths were held equal, and the eight methylene CH bond lengths were held equal. The structure obtained has β = 70.0° and an NN distance of 2.52 Å, as compared with a MINDO/3 calculation of C_{3v} Dabco having β = 47.9° and an NN distance of 2.408 Å (E. Haselbach, private communication).

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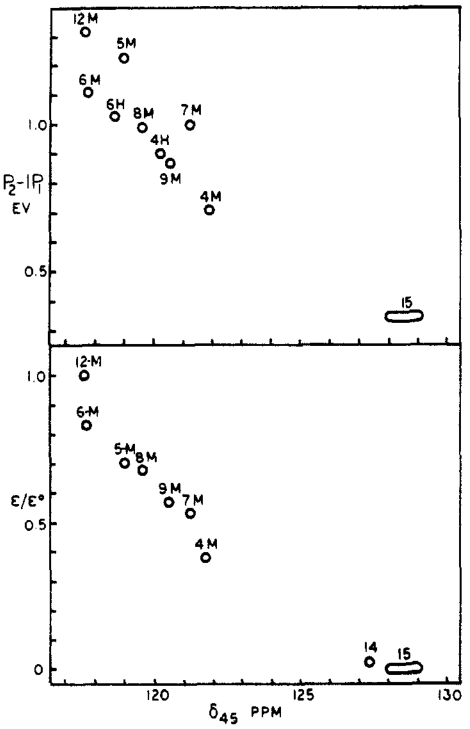
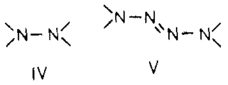


Figure 7. Plots of $IP_2 - IP_1$ (above) and ϵ/ϵ^0 (below) vs. chemical shift of $C_{4,5}$ ($\delta_{4,5}$) from (Me_4Si). The points are identified by compound numbers: 12M = 12-Me, etc.

The carbon NMR shift (δ_{45}), ϵ/ϵ^0 (see the Discussion in ref 1) and $IP_2 - IP_1$ all are rough measures of the lone pair–aryl ring interaction, but the plots in Figure 7 indicate that their correlation shows significant scatter. They clearly respond somewhat differently to the θ and β changes between different compounds. MINDO/3 calculations of charge density are known not to be accurate enough for correlations of ^{13}C chemical shifts, but such calculations predict that changing β from 20° to 50° at $\theta = 0°$ changes the excess charge at C_{45} to almost half as much as the total amount of charge when θ is changed from 0 to −90° (con). This suggests that δ_{45} is probably more sensitive to changes in β than is $IP_2 - IP_1$, but we have been unable to use the correlations of Figure 7 to separate the θ and β effects on lone pair–aryl ring interaction and obtain conformational information. Only quite general statements such as that 4-Me has a smaller lone pair–aryl interaction than any of the monocyclic bridged compounds 5-Me to 9-Me and that 4-Me has a smaller interaction than 4-H can presently be made.

$E°'$–IP_1 Correlation. The vertical IP_1 values reported here allow correction of the adiabatic $E°'$ data reported earlier[1] for the effect of the energy of the HOMO which has been previously discussed in detail for tetraalkylhydrazines (IV) and tetraalkyl-2-tetrazenes (V).[4] Selected



IV V

examples of I and IV are compared in an $E°'$ vs. IP_1 plot in Figure 8. As expected, considerably greater IP_1 changes are observed for I than for IV as the heterocyclic ring size is changed; larger changes in both θ and β are occurring for I. In addition to and considerably more important than the influence of HOMO energy, $E°'$ is influenced by changes in steric interactions when the structure changes upon electron removal. For a series of normal alkyl V derivatives, where different steric effects are minimized, a plot of $E°'$ vs. IP_1 had a slope of 0.21 in acetonitrile.[4c] The low slope is the result of the loss of polarization effects for alkyl group stabilization in solution[17] and solvation energy effects (decreases solvation stabilization of the cationic form with longer alkyl groups). When the HOMO energy is changed by changing the size of fused aromatic systems, the $E°'$ vs. IP_1 plot has a slope much closer to 1, i.e., 0.89 in acetonitrile.[18]

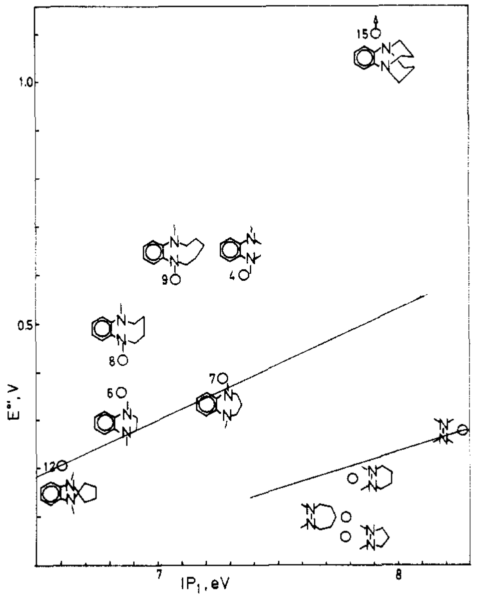


Figure 8. $E°'$ vs. IP_1 plot for selected *o*-phenylenediamines (4-Me, 6-Me, 7-Me, 12-Me, and 15, where $E°'$ was not measured but E_p^{ox} used as a minimum value) in butyronitrile and for hydrazines in acetonitrile.

For the extensively studied IV derivatives,[4] allowing for HOMO effects was best accomplished by using an $E°'$ vs. IP_1 slope of 0.15 and gave internally consistent and reasonable results for many compounds, even when the majority of the IP_1 change resulted from a different θ' value than that of the model compound, tetramethylhydrazine. By comparison of $E°'$ for tetramethylhydrazine with that for 1,1'-bis(pyrazolidine) (and many others), it was concluded that a steric destabilization for tetramethylhydrazine of about 2.6 kcal/mol per methyl–methyl interaction resulted from the change in geometry which occurs when an electron is removed.

Performing a similar analysis on the I data, we draw a hypothetical HOMO-effect line with a slope of 0.21 through the 12-Me point of Figure 8, arguing that little change in steric interactions can occur for this compound, which has the nitrogens essentially flat in the neutral form. The observed $E°'$ for 4-Me is 0.23 V (5.3 kcal/mol) above the line ($E°'$ (correlation) = 0.21 IP_1 − 1.18 V), suggesting a steric destabilization in $(4\text{-Me})^{+\cdot}$ of 5.3 kcal/mol. It is obvious from the structure of 4-Me that when an electron is removed and the cation tries to become planar, the methyl–methyl interaction is considerably more serious than that in the tetramethylhydrazine radical cation; the number obtained seems plausible. Although a true $E°'$ for 15 is not available, the E_p^{ox} of 1.1 V is negative of $E°'$ if the electron-transfer rate remains relative to the scan rate, as we expect. This leads to an estimate that $15^{+\cdot}$ is destabilized by ≥0.61 V (14.1 kcal/mol) relative to $(12\text{-Me})^{+\cdot}$. We argue that this provides at least a rough experimental measure of the amount of stabilization produced by lone

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pair-aryl interaction in an unstrained example of I$^{+\cdot}$.

Both **6**-Me and **7**-Me fall only slightly above the correlation line (2.3 and 0.9 kcal/mol, respectively), but the interplay between effects on the neutral and cationic forms is of course not clear. The effect of 3,6-dimethyl substitution on ground-state conformation is substantial, but changes in $E^{\circ\prime}$ deviation from the correlation line are small. **4A**-Me is only 0.6 kcal/mol more difficult to oxidize in solution than is **4**-Me when adjustments for HOMO energy are made by using the correlation line. In contrast, 4,5-dimethyl substitution should not affect the conformation significantly, but the **4B**-Me deviation is −1.3 kcal/mol from the value for **4**-Me. Methylating the benzene ring causes a larger increment in $E^{\circ\prime}$ than is accounted for in employing the correlation line. This would occur if solvation energy differences were significant and is consistent with data on para-substituted dimethylanilines, which show a slope greater than 1 in an $E^{\circ\prime}$ vs. IP$_1$ plot.[18]

Our data make it clear that quantitative interpretation of $E^{\circ\prime}$ differences is full of pitfalls for the unwary.

Experimental Section

Compound preparations are mainly described in the earlier paper.[1]

1,3,5,6-Tetramethyl-2,2-tetramethylenebenzimidazole [(12B-Me). A mixture of 1.0 g (6.1 mmol) of 4,5-dimethyl-*N*,*N'*-dimethyl-*o*-phenylenediamine, 5.1 g (61 mmol) of cyclopentanone, and 10 mL of toluene was refluxed on a water separator for 6 h, concentrated, and Kugelrohr distilled (0.02 torr, 150 °C), giving 1.08 g (80%) of a yellow oil: ^{1}H NMR δ 5.80 (s, 2 H), 2.61 (s, 6 H), 2.06 (s, 6 H), 1.4–3.0 (m, 8 H); empirical formula determined by high-resolution mass spectroscopy.

Photoelectron spectroscopy measurements were made on a Varian 1EE-15 instrument, and the data were handled as previously described.[3] A picture of each photoelectron spectrum appears in the thesis of L.A.G.[19] Calculations were performed on a Harris/7 computer.

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Registry No. **4**-H, 95-54-5; **4**-Me, 704-01-8; **4A**-Me, 66102-30-5; **4B**-H, 3171-45-7; **4B**-Me, 54929-05-4; **5**-Me, 3204-31-7; **6**-H, 3476-89-9; **6**-Me, 2427-06-7; **6A**-H, 66102-39-4; **6A**-Me, 66102-31-6; **6B**-H, 10579-68-7; **6B**-Me, 66102-32-7; **7**-H, 6516-89-8; **7**-Me, 19560-66-8; **8**-H, 39161-58-5; **8**-Me, 39161-60-9; **9**-Me, 66102-33-8; **12**-Me, 66102-34-9; **12B**-Me, 75751-20-1; **14**, 7140-45-6; **14A**, 66102-38-3; **14B**, 66102-37-2; **15**, 73023-02-6; 4,5-dimethyl-*N*,*N'*-dimethyl-*o*-phenylenediamine, 75751-21-2; cyclopentanone, 120-92-3.

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Hydrozirconation of Thioketones. A Simple, Convenient Entry into a Variety of Organosulfur Compounds. An Interesting Ether Synthesis

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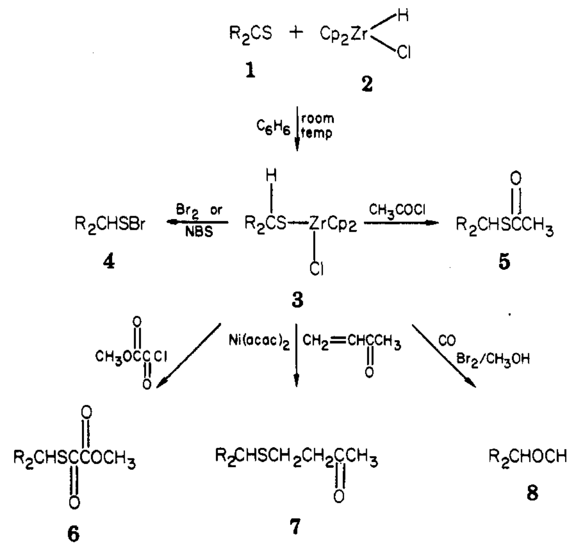
Aromatic and aliphatic thioketones undergo hydrozirconation at room temperature with $(C_5H_5)_2Zr(H)Cl$ to give sulfur–zirconium compounds, $R_2CHSZr(Cl)(C_5H_5)_2$. Cleavage of the latter by bromine or *N*-bromosuccinimide affords sulfenyl bromides, acid chlorides give thioesters, methyloxalyl chloride gives a thiooxalate, methyl vinyl ketone [catalyzed by Ni(II)] results in the formation of the β-keto sulfide, and carbonylation followed by bromination in alcohol affords the ether. Very mild conditions are utilized for all of these reactions. Mechanisms are proposed for the interesting ether synthesis.

The past 10 years have witnessed an increased awareness of the importance of transition-metal organometallic compounds as reagents for organic synthesis.[2] Of the many such reagents developed during this period, hydridochlorobis(cyclopentadienyl)zirconium is one of the most important. Excellent work by Schwartz and co-workers[3] has demonstrated that facile hydrozirconation of olefins affords organozirconium species which can undergo subsequent cleavage by various reagents (peroxide, halogen, etc.) to give useful organic products.

We have, for some time, been examining the chemistry of thioketones in terms of applications to organic synthesis[4] and to the preparation of novel organometallic complexes.[5] It seemed conceivable that thioketones should, like olefins, experience hydrozirconation and that sulfur–zirconium bond cleavage of the generated zirconium intermediate may constitute an entry into a variety of interesting or-

Scheme I



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