fast as carbonate ions do,[44] we neglected catalysis by carbonate ions.

The methylamine buffer solutions were prepared from standard solutions of methylamine, methylammonium chloride, hydrochloric acid, and sodium hydroxide with sodium chloride added as needed to bring the ionic strength into the range 0.197 ± 0.008 M. In all cases the pH was measured before the addition of acetone-d_6. After the first runs were made it was noted that addition of the acetone decreased the pH (by 0.10 ± 0.02) and, later, that the pH of the solutions usually increased by a few hundredths of a pH unit during the course of the run. The pH used in our calculations was that taken during (or after) the run if a value was taken or 0.10 less than the pH of the buffer without acetone (preferably determined during or after the run).

The second-order rate constants reported have been corrected for thermal expansion or contraction of the reaction solution as well as for the volume change that accompanied the addition of acetone.

pK Determinations. The pK values of 1,4-diazabicyclo[2.2.2]-octane were determined by titration of 16 ml of a 0.07 M solution with 1.0047 M hydrochloric acid using apparatus[45] and methods of calculation[46] described previously. The thermodynamic pK values for the monoprotonated and diprotonated species were determined from data in the ionic strength ranges 0.015–0.045 and 0.107–0.155, respectively. These values, 8.77 ± 0.02 and 2.78 ± 0.01, respectively, showed no clear trend with changing ionic strength. These are comewhat higher than the values 8.65 and 2.67 that may be obtained from earlier data at 25° and ionic strength 0.1 M[47] by use of the Davies equation[46] and the calorimetrically determined enthalpies of reaction.[47]

---

[44] C. D. Gutsche, D. Redmore, R. S. Buriks, K. Nowatny, H. Grassner, and C. W. Armbruster, *J. Amer. Chem. Soc.*, **89**, 1235 (1967).

[45] J. Hine and F. C. Kokesh, *ibid.*, **92**, 4383 (1970).

[46] J. Hine, F. A. Via, and J. H. Jensen, *J. Org. Chem.*, **36**, 2926 (1971).

[47] P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, **69**, 3759 (1965).

Bonding Studies in Group IV Substituted Anilines. I. A Comparison of Charge-Transfer and Electrochemical Methods for Determining Ground-State Energies

Paul Ronald Jones,* Michael J. Drews, Jerry K. Johnson, and Pui Suen Wong

Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203. *Received October 19, 1971*

Abstract: The energies of the long-wavelength transitions for charge-transfer complexes and the electrolytic half-peak oxidation potentials ($E_{P/2}$) are reported for a series of substituted anilines including *p-tert*-butyl-, *p*-trimethylsilyl-, *p*-trimethylgermyl-, and *m*-trimethylsilyl-*N,N*-dimethylaniline. The charge-transfer spectra do not provide reliable measurements of the relative energies of the ground-state molecular orbitals for this series of compounds. Correlations between $E_{P/2}$ values and ionization potentials determined by photoelectron spectroscopy are used to calculate ionization energies for the anilines. The results indicate a small stabilization of the highest filled molecular orbital (HFMO) when silicon or germanium is substituted for carbon in the para position of *N,N*-dimethylaniline.

In 1934 Koopmans proposed that the energy of the highest occupied molecular orbital of a molecule is equal to the negative of the observed molecular ionization energy.[1] Because the energy of a molecular orbital reflects the overall perturbation of that orbital by substituents, the ionization energies of a series of closely related molecules provide a basis for comparing substituent effects on their ground-state orbitals. While direct measurements of the ionization energies of larger molecules are rather difficult and expensive to obtain, electrolytic oxidation potentials and intermolecular charge transfer band maxima, both of which may be related to the ionization energy of a molecule, are readily determined.

The energy of the long-wavelength transitions for weak complexes between donors (D) and acceptors (A) has been related to the ionization potential of the donor (I^D) and the electron affinity of the acceptor (E^A) by Mulliken using perturbation theory, eq 1,[2] where $G_1 - G_0$ represents the difference in energy between the coulombic attraction in the excited state (G_1) and the van der Waals interaction in the ground state (G_0) of the complex, and β_0^2 and β_1^2 are intermolecular resonance terms in the ground and excited states, respectively. With the assumption that the terms $G_1 - G_0$ and $\beta_0^2 + \beta_1^2$ are constant for a series of complexes of different donors with the same acceptor, eq 1 may be somewhat simplified, but remains a parabolic relationship between $h\nu_{CT}$ and I^D.[3] McConnell and coworkers have demonstrated that an empirical linear relationship between $h\nu_{CT}$ and I^D, eq 2, is applicable to a wide variety of complexes.[4] Although it has been pointed out that

$$h\nu_{CT} = a_{CT}I^D + b_{CT} \qquad (2)$$

there is no theoretical justification for such a linear relation,[5] it has been applied to the estimation of ionization potentials for a large variety of donors and acceptors with considerable success.[6–8]

$$h\nu_{CT} = I^D - (E^A + G_1 - G_0) + \frac{\beta_0^2 + \beta_1^2}{I^D - (E^A + G_1 - G_0)} \qquad (1)$$

---

[1] T. Koopmans, *Physica*, **1**, 104 (1934).

[2] R. S. Mulliken, *J. Amer. Chem. Soc.*, 72, 600 (1950); 74, 811 (1952).

[3] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959).

[4] H. McConnell, J. S. Ham, and J. F. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[5] R. S. Mulliken and W. B. Person, *Annu. Rev. Phys. Chem.*, **13**, 107 (1962).

[6] See, for example, R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, and references therein.

[7] H. Bock and H. Alt, *J. Amer. Chem. Soc.*, **92**, 1569 (1970).

[8] H. Bock and H. Alt, *J. Organometal. Chem.*, **13**, 103 (1968).

Table I. Charge-Transfer Band Maxima for $Me_2NC_6H_5X^a$

Compd no.	Substituent X	TCNE, 25°	TCNE, −60 to −80°		Chloranil, 25°	
		$h\nu_{CT}$, eV	$h\nu_{CT}$, eV	$\Delta\nu_{1/2}$, cm^{-1}	$h\nu_{CT}$, eV	$\Delta\nu_{1/2}$, cm^{-1}
1	H	1.826	1.929	5500	1.883	5300
2	*p*-Me_3C	1.802	1.864	4600	1.850	5100
3	*p*-Me_3Si	1.807	1.867	4900	1.844	5400
4	*p*-Me_3Ge	1.806	1.864	*c*	*c*	
5	*m*-Me_3Si	1.847^b	*c*		*c*	

[a] Determined in methylene chloride using excess acceptor. [b] $\Delta\nu_{1/2}$ = 5250 cm^{-1}. [c] Not determined.

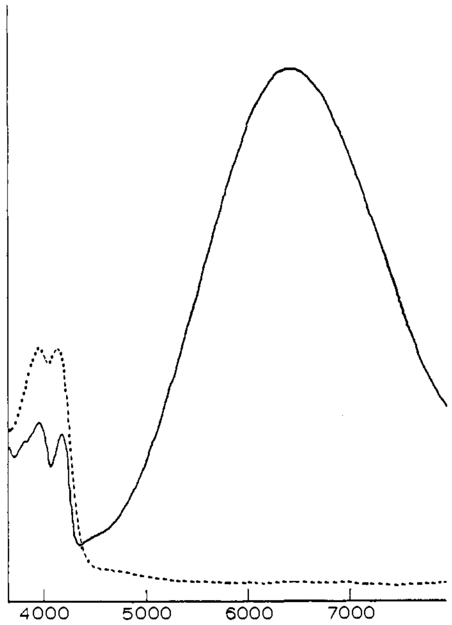


Figure 1. Visible spectrum of the charge-transfer complex of *m*-trimethylsilyl-*N*,*N*-dimethylaniline with TCNE at room temperature in methylene chloride (——) and TCNE alone (-----).

A linear relationship also obtains between electrolytic oxidation potentials ($E_{1/2(\mathrm{ox})}$) and the ionization potentials of molecules, eq 3,[9] where ΔE_{sol} is the difference

$$E_{1/2(\mathrm{ox})} = I + \Delta E_{\mathrm{sol}} - \frac{T\Delta S^\circ}{\mathcal{F}} - \frac{RT}{\mathcal{F}} \ln \frac{f^+D}{fD^+} + \text{constant} \qquad (3)$$

in solvation energy between the compound and its cation, f^+ and f are the activity coefficients of the ion and the neutral molecule, and D^+ and D are their respective diffusion coefficients. For a series of similar compounds, ΔE_{sol} may be assumed to be constant or a linear function of I, and the logarithmic term will be small. Variations in the other terms will be small with respect to I and the relation may be rewritten, eq 4.

$$E_{1/2(\mathrm{ox})} = a_{\mathrm{E}}I + b_{\mathrm{E}} \qquad (4)$$

While strict application of eq 3 requires total reversibility for the electrode reaction, it has been noted that there is a linear relationship between the $E_{P/2}$ obtained by cyclic voltammetry and $E_{1/2}$.[10] Further, all that is required to apply eq 4 is a series of related compounds which behave similarly, and give values which are reasonably close to reversible oxidation potentials, conditions met in most studies.[11] One obvious advantage of the electrochemical technique compared to the charge-transfer method for determining ionization potentials is the theoretical justification for a linear relationship between $E_{1/2(\mathrm{ox})}$ and I.

We have determined the band maxima for charge-transfer complexes and electrolytic oxidation potentials for a series of group IVA substituted and related *N*,*N*-dimethylanilines in order to assess the effect of group IV substituents on the bonding levels of the molecules.

Results

Charge-Transfer Complexes. The energies of the long-wavelength transitions for the charge-transfer complexes of *N*,*N*-dimethylaniline (**1**), *p*-*tert*-butyl- (**2**), *p*-trimethylsilyl- (**3**), *p*-trimethylgermyl- (**4**), and *m*-trimethylsilyl-*N*,*N*-dimethylaniline (**5**) were determined in methylene chloride using tetracyanoethylene (TCNE) or chloranil as acceptors. In order to improve the stability of the complexes of *N*,*N*-dimethylaniline and the para-substituted compounds with TCNE, their spectra were also determined at low temperature (−60 to −80°). Figure 1 illustrates a typical spectrum. The two bands at ~4000 Å are attributed to transitions of the TCNE radical anion.[12] The presence of TCNE·⁻ was confirmed with an esr spectrum of the complex which consisted of a nine-line spectrum, with a separation of 1.55 G, expected for TCNE·⁻.[13] These higher energy transitions were not present in the spectra of the charge-transfer complexes with chloranil.

The half-height widths ($\Delta\nu_{1/2}$) of the charge-transfer bands were in the range 4000–6000 cm^{-1}, typical of single charge-transfer processes.[14] The separation of the two highest occupied molecular orbitals for *N*,*N*-dimethylaniline is on the order of 1.5 eV[15] or about 5150 Å. It is reasonable to conclude that the charge-transfer energies listed in Table I are transitions from single energy levels in the donors, not overlapping multiple transitions, and that any transitions which occur from lower lying molecular orbitals of the donors will be found in the ultraviolet region of the spectrum.

Inspection of Table I reveals that the energy of the charge-transfer band is rather insensitive to the nature of the substituent in the para-substituted compounds. This result is rather surprising in view of the sensitivity of the band energy to para substituents which has been observed by other workers under similar experimental conditions.[16] The possibility that the similarity of ener-

---

(9) E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963).

(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 709 (1964).

(11) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, p 327.

(12) O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

(13) W. D. Phillips, J. D. Powell, and S. I. Weissman, *J. Chem. Phys.*, 33, 626 (1960).

(14) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969, p 89.

(15) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).

(16) N. S. Isaacs, *ibid.*, 1053 (1966).

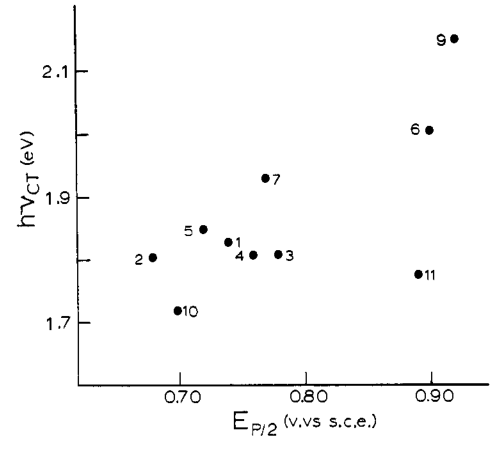


Figure 2. Plot of the energies of the charge-transfer band maxima against the electrolytic oxidation potentials.

gies may be due to decomposition is ruled out by the low-temperature experiment. Under these conditions the spectra of the complexes remain unchanged for several hours, yet the position of the charge-transfer bands for compounds **2**, **3**, and **4** does not vary significantly.

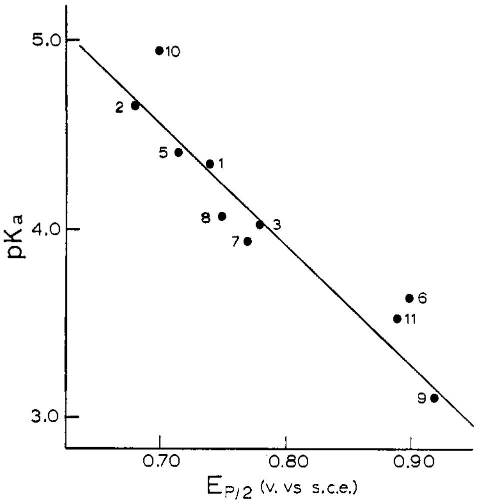


Figure 3. Plot of the basicities of the anilines against the electrolytic oxidation potentials.

Oxidation Potentials. The oxidation potentials of the compounds listed in Table II were determined by cyclic voltammetry in acetonitrile solution using tetrabutylammonium perchlorate as the supporting electrolyte. When consecutive runs were made on the same solutions for compounds **1**–**4**, additional anodic and cathodic peaks began to appear at +0.35, +0.53 V and +0.29, +0.47 V, respectively. These new peaks have been assigned to *N*,*N*,*N*′,*N*′-tetramethylbenzidine formed from the decomposition of the initially formed radical cation.[17] In studies of the esr spectra of the radical cations, the initially observed spectrum of the radical cation decays with time and the final spectrum obtained in the electrolytic oxidation of compounds **1**–**4** is that of *N*,*N*,*N*′,*N*′-tetramethylbenzidine radical cation.[18] The appearance of additional product waves in the voltammogram did not affect the potentials of the waves observed on the initial sweep appreciably. Table II lists the half-peak potential data obtained. Comparison of the $E_{P/2}$ results with those obtained for the charge-transfer experiments indicates that the electrochemical technique is appreciably more sensitive to the nature of the substituent for the group IV substituted anilines.

Table II. Comparison of the Experimental Ground-State Properties for XC_6H_4Y

Compd no.	Substituents X	Y	$E_{P/2}$[a] V *vs.* sce	$h\nu_{CT}$,[b] eV	pK_a
1	H	NMe_2	0.74	1.826[c]	4.35[d]
2	*p*-Me_3C	NMe_2	0.68	1.802	4.65[d]
3	*p*-Me_3Si	NMe_2	0.78	1.807[c]	3.98[d]
4	*p*-Me_3Ge	NMe_2	0.76	1.806	
5	*m*-Me_3Si	NMe_2	0.72	1.847	4.41[d]
6	H	NH_2	0.90	2.034[e]	3.63[f]
7	H	NHMe	0.77	1.928[e]	3.93[f]
8	*p*-Me	NH_2	0.75		4.06[f]
9	*p*-Cl	NH_2	0.92	2.145[e]	3.10[f]
10	*p*-Me	NMe_2	0.70[g]	1.717[e]	4.94[d]
11	*p*-Br	NMe_2	0.89	1.773[e]	3.52[d]

[a] Determined in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. [b] TCNE acceptor in methylene chloride. [c] 1.823 and 1.761 have been obtained by other workers for **1** and **3**, respectively (H. Alt, Ph.D. Thesis, Ludwig Maximilian University, Munich, Germany, 1969, p 158). [d] Reference 21. [e] Determined under conditions identical with ours by N. S. Isaacs, *J. Chem. Soc. B*, 1053 (1966). [f] Calculated as described in the Experimental Section from data given by Perrin.[22] [g] M. Melicharek and R. F. Nelson, *J. Electroanal. Chem. InterfacialElectrochem.*, **26**, 201 (1970).

If both the energy of the long-wavelength charge-transfer band and the electrolytic oxidation potential of a molecule are linearly related to the molecular ionization energy, a linear relation between $h\nu_{CT}$ and $E_{P/2}$ should exist.[9] The observed half-wave potentials are plotted against the long-wavelength transition energies for the TCNE complexes in Figure 2. The linear relation between $h\nu_{CT}$ and $E_{P/2}$ commonly observed in other systems[9,19] apparently does not apply to the substituted anilines in this study.

Correlations with Base Strength. The base strengths of substituted anilines have been correlated with the energies of the highest filled molecular orbital by Latta and Taft.[20] Isaacs has discussed the linear relationship between the pK_a and $h\nu_{CT}$ for a variety of aromatic amines.[16] Benkeser has related the pK_a values of a series of silyl-substituted aromatic amines to the inductive and d orbital effects of silicon.[21] Table II lists the pK_a values for the anilines involved in this study. These pK_a values are either those reported by Benkeser,[21] or estimated from data given by Perrin.[22] The linear relation between these base strengths and the oxidation potentials of the anilines is shown in Figure 3. The root-mean-square deviation of the points from the calculated straight line shown is 0.18. Such a correlation is good evidence that, for the group IV substituted anilines, electrolytic oxidation potentials are more closely related to ground-

---

(17) R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

(18) P. R. Jones, M. J. Drews, and P. S. Wong, unpublished results.

(19) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, Chapter 7.

(20) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

(21) R. A. Benkeser and H. A. Krysiak, *ibid.*, **75**, 2421 (1953).

(22) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965; J. Clark and D. D. Perrin, *Quart. Rev., Chem. Soc.*, **18**, 295 (1964).

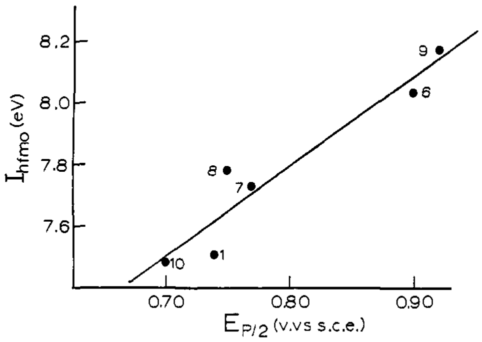


Figure 4. Plot of ionization energies measured from photoelectron spectra[15] and electrolytic oxidation potentials.

state properties than are the energy maxima for charge-transfer complexes. This result also suggests that the molecular orbital from which the electron is removed on oxidation has a significant density at nitrogen, or possesses considerable n character. This conclusion is supported by the large nitrogen hyperfine coupling constants observed in the esr spectra of the radical cations of these molecules.[18,20]

Ionization Energies. The photoelectron spectra of several of the anilines involved in this study have been determined by Turner and coworkers.[15] Figure 4 is a plot of the vertical ionization energies of the HFMO reported by Turner and the electrolytic oxidation potentials obtained in this study. The straight line indicated is the best least-squares fit of the data and has eq 5, where I is given in electron volts and $E_{P/2}$ is in volts

$$I = 2.95E_{P/2} + 5.44 \qquad (5)$$

vs. sce. The agreement in Table III between the experimental values of the ionization energies and those calculated from eq 5 is well within the limits of experimental error, with a standard deviation between the experimental and calculated values of 0.08 eV.

Table III. Experimental and Calculated Ionization Energies

Compd no.	Ionization energy, eV Exptl[a]	 Calcd
1	7.51	7.62
2		7.44
3		7.74
4		7.68
5		7.56
6	8.04	8.09
7	7.73	7.71
8	7.78	7.65
9	8.18	8.15
10	7.48	7.50
11		8.06

[a] Reference 15.

Discussion

The lack of correlation between energies of the charge-transfer band maxima and ionization potentials is not wholly unanticipated. It may be noted in Figure 2 that those anilines which show the greatest deviation from a "linear" relationship are those in which a mesomeric interaction of the substituent with the aromatic π system might be expected. Mulliken has estimated that such delocalization of charge in the charge-transfer complexes can vary the value of G_1 in eq 1 by as much as 0.9 eV,[23] an uncertainty significantly greater than the variation in the charge-transfer energies listed in Table II. The results indicate the great danger in using charge-transfer spectra alone to estimate energies of ground-state molecular orbitals.

The calculated ionization energies listed in Table III show that there is a small but real stabilization of the highest filled molecular orbital when silicon or germanium is substituted for carbon in the para position of *N*,*N*-dimethylaniline. Whether it is more appropriate to attribute this stabilization to d orbital interaction or to a hyperconjugative σ–π interaction will be discussed in a subsequent paper.

Experimental Section

Reagents. The solvents used for the organometallic reactions were distilled from lithium aluminum hydride prior to use and all such reactions were carried out under an atmosphere of dry nitrogen or argon. Acetonitrile was purified using a modification of the method given by Mann,[24] in which the final purification step was distillation of the solvent from phosphorus pentoxide. Tetrabutylammonium perchlorate (Matheson Coleman and Bell, polarographic grade) was dried *in vacuo* at 78° over phosphorus pentoxide. The water content of the typical solution, determined by the method of Osa and Kuwana,[25] was less than 5 m*M*. Methylene chloride and carbon tetrachloride (Matheson Coleman and Bell, spectroquality) were used without further purification.

Tetracyanoethylene (Aldrich) was purified by vacuum sublimation and chloranil (Eastman) was recrystallized from benzene prior to use.

All the anilines were purified by gpc collection using a 20 ft × $^3/_8$ in. stainless steel column of 20% Carbowax 20M on 45–60 mesh Chromosorb W at 210° with a flow rate of He of 145 ml/min, for characterization and prior to the measurements made in this study.

***p*-Trimethylsilyl-*N*,*N*-dimethylaniline (3)** (bp 101° (1.3 Torr)) was prepared in 70% yield by the method of Gilman and Marshall.[26]

Anal. Calcd for $C_{11}H_{19}NSi$: C, 68.31; H, 9.82; N, 7.24; mass, 193. Found: C, 68.07; H, 9.94; N, 7.46; mass spectrum, parent (M^+), 193.

***m*-Trimethylsilyl-*N*,*N*-dimethylaniline (5)** (bp 113–115° (10 Torr)) was synthesized using the procedure of Benkeser and Krysiak[21] in 79% yield.

Anal. Found: C, 68.57; H, 10.24; N, 7.08; mass spectrum, parent (M^+), 193.

***p*-*tert*-Butyl-*N*,*N*-dimethylaniline (2)** (bp 125° (16 Torr)) was prepared from *tert*-butylbenzene using the method of Davies and Hulbert.[27]

Anal. Calcd for $C_{12}H_{19}N$: C, 81.36; H, 10.73; N, 7.91; mass, 177. Found: C, 81.24; H, 11.21; N, 7.78; mass spectrum, parent, 177.

***p*-Trimethylgermyl-*N*,*N*-dimethylaniline (4).** To a solution of 6.08 g (30.4 mmol) of *p*-bromo-*N*,*N*-dimethylaniline (Eastman, practical grade) in dry benzene was added 24.5 ml (30.4 mmol) of a solution of 1.24 *M* *tert*-butyllithium in pentane (Foote Mineral),[28] and the mixture was stirred under dry nitrogen for 1.5 hr. The reaction mixture was cooled to 0° and 5 g (25.3 mmol) of trimethylgermanium bromide in 20 ml of tetrahydrofuran was added dropwise. After stirring overnight at room temperature, the mixture was hydrolyzed with water and the organic layer separated, combined with ether washings of the aqueous layer, dried over anhydrous magnesium sulfate, and distilled to give 2.58 g (42% yield) of product: bp 123° (5 Torr); nmr (CCl_4 with TMS as the internal

---

(23) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969, p 123.

(24) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).

(25) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).

(26) H. Gilman and F. J. Marshall, *J. Amer. Chem. Soc.*, **71**, 2066 (1949).

(27) W. C. Davies and F. L. Hulbert, *J. Soc. Chem. Ind.*, **57**, 349 (1938).

(28) If *n*-butyllithium was used as the metallating agent in this reaction, the *p*-*n*-butyl-*N*,*N*-dimethylaniline which is produced as a side product could not be separated from the desired germyl compound.

standard) δ -0.31 (s, 9 H, $(CH_3)_3Ge$), -2.83 (s, 6 H, $(CH_3)_2N$), -6.48 and -7.11 (d, 4 H, aromatic protons, $J = 8$ Hz).

Anal. Calcd for $C_{11}H_{19}NGe$: C, 55.54; H, 8.05; N, 5.83. Found: C, 55.37; H, 8.29; N, 6.16.

The other anilines were all obtained from commercial sources.

Charge-transfer spectra were recorded on a Cary-14 spectrophotometer. The low-temperature apparatus consisted of a jacketed cell mounting through which a stream of cooled nitrogen gas was passed. The temperature was controlled by varying the rate of nitrogen flow and was constant to ±5°. These slight variations in temperature had negligible effects on the charge-transfer spectra below $-50°$. The entire cell compartment was purged with dry nitrogen to prevent water condensation at the low temperatures.

For the room temperature spectra, 5-10 μl of the aniline were added to 3 ml of a solution 10^{-3} *M* in acceptor in 10-mm quartz sample cells and the spectra determined immediately. Using this technique, spectra could be recorded before significant decomposition occurred. For the low-temperature work, because of increased complex formation and slower decomposition, about 0.1 μl of the aniline was sufficient to obtain satisfactory spectra. The results are tabulated in Table I.

Oxidation potentials were determined by cyclic voltammetry using a standard three-electrode cell consisting of a platinum button working electrode (Beckman, 39273), a saturated calomel reference electrode, and a platinum coil as the counter electrode. The potential sweep was provided by a Chemtrix 300 polarographic amplifier with type 205 polarographic time-base plug-in units. A Keithley 602 electrometer was used to calibrate the starting potentials and the measurements were recorded using a Tektronix 564 storage oscilloscope equipped with a Polaroid camera.

In a typical run a solution 10^{-4} *M* in sample and 0.1 *M* in tetrabutylammonium perchlorate was maintained under an atmosphere of dry argon throughout the measurement. A rate of 0.100 V/sec was employed scanning a 1.00-V range. The average deviation of $E_{P/2}$ values measured in separate runs was ±0.01 V.

Estimation of pK_a Values. The basicities of the anilines reported by Benkeser[21] were determined in 50% aqueous ethanol. In order to compare these values with those obtained for aqueous solutions[22] the equation, $pK_{a(EtOH-H_2O)} = pK_{a(aq)} + C$, was used. For anilines studied by both workers the constant, *C*, had a value of approximately -1.0 p*K* unit.

Acknowledgment. The authors wish to thank the Robert A. Welch Foundation, the Research Corporation, and the Faculty Research Fund of North Texas State University for the financial support of this work.

Chemistry of Diradicals. III. Calculation of Spin Correlation Effects on the Rotational Barriers in 1,4 Diradicals

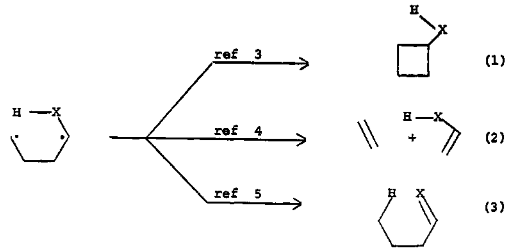
L. M. Stephenson* and Thomas A. Gibson

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received October 4, 1971*

Abstract: The C_1–C_2 or C_3–C_4 bond rotational barriers are calculated for the singlet and triplet 1,4 diradical species. Substantially higher barriers are found for the singlet diradical as compared to the triplet diradical or other model systems. These trends are discussed in terms of simple molecular orbital and valence bond concepts. It is postulated that variable bond rotational barriers are capable of rationalizing the quantitative features of 1,4 diradical chemistry.

In this paper, molecular orbital concepts will be used in an attempt to understand the influence of the nonbonded radical centers on rotational barriers in diradical species. As we have previously pointed out,[1] reasonably accurate estimates of bond rotational barriers are critically important to a quantitative description of diradical systems; variations in estimated thermochemical quantities lead to startlingly different theoretical descriptions of the 1,3 and 1,4 diradical systems.[1–3]

Experimental studies of diradicals, and, in particular, reports of spin correlation effects in the reactions of these systems, have been frequent in recent years. Common features have been noted in nearly all contributions. Thus, in the 1,4 diradical species, high stereospecificity is noted in singlet manifolds while triplet diradicals show little or no selectivity in typical reactions,[3–5] such as eq 1–3. These differences in stereoselectivity have been attributed to the longer lifetimes of the triplet species, which are required to intersystem cross (to singlet species) before bond forming events can occur.[3] Despite the attractiveness of this explanation, comparison of these results with older work on cyclobutane pyrolyses[6,7] has led us to point out several apparent inconsistencies and to propose an alternative explanation.[1] Briefly, the following points from this treatment may be summarized. The pyrolysis of 1,2-dimethylcyclobutane is consistent with the intermediacy of 1,4 diradicals which encounter activation barriers to closure or cleavage reactions of 6–8 kcal/mol leading to generalized potential energy surfaces such as that shown in Figure 1. This description then requires bond rotational barriers approaching the



---

[1] Paper II in this series is L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

[2] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

[3] P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

[4] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, **93**, 1984 (1971).

[5] N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

[6] H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 4884 (1961).

[7] E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).