

The results shown in Figure 13 indicate a lower dipole moment for the 1L_a state than for 1L_b . One should bear in mind that the so-called 1L_a transition is no longer a strong $\pi \rightarrow \pi^*$ transition; the large amount of charge-transfer character has reduced its transition moment, and thus $\bar{\mu}({}^1L_a) < \bar{\mu}({}^1L_b)$ is reasonable in this particular case. The 1L_a state is also strongly solvent sensitive, and its $|\bar{\mu}|$ value increases with solvent polarity after the inversion; hence there is no doubt that 1L_a of 1,5-DNS is a polar state.

In Figure 13, most of those points which deviate from the curves are for solvents where solubility problems were encountered. Error arises from measurement of k_f and $\bar{\nu}_f$ since these values are extrapolated instead of being measured directly. For instance, 1,5-DNSA has low solubility in water; the measurements of ϕ_f , τ_f , and $\bar{\nu}_f$ were done by extrapolating from water-ethanol mixtures; the very low value of ϕ_f and τ_f also will cause a high percentage of error, which will be multiplied in the calculation of $|\bar{\mu}|$.

Calculated values of $|\bar{\mu}^{el}_{S_1 \rightarrow S_0}|/e$ values of 2,6-DNS range from 0.54 Å in nonpolar solvents to 0.57 Å in water. Unfortunately there is no direct comparison with Brand's $|\bar{M}^{el}_{S_1 \rightarrow S_0}|/e$ value,¹³ however, by estimating this value,¹³ it should be about 0.40 Å. Therefore, because $|\bar{\mu}^{el}_{S_1 \rightarrow S_0}|/e$ is greater than $|\bar{\mu}^{el}_{S_1 \rightarrow S_0}|/e$, the excited-state dipole moment is indeed larger than that of the ground state. The calculated $|\bar{\mu}^{el}_{S_1 \rightarrow S_0}|/e$ for 1,5-DNS is 0.54 Å for 1L_b and 0.48 Å for 1L_a .

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References and Notes

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- (2) (a) L. Stryer, *J. Mol. Biol.*, **13**, 482 (1965); (b) W. O. McClure and G. M. Edelman, *Biochemistry*, **5**, 1908-1919 (1966); **6**, 559-566 (1967); **6**, 567-572 (1967).
- (3) R. F. Chen and J. C. Kernohan, *J. Biol. Chem.*, **242**, 5813-5823 (1967).
- (4) L. Stryer, *Science*, **162**, 526-533 (1968).
- (5) G. M. Edelman and W. O. McClure, *Acc. Chem. Res.*, **1**, 65 (1968).
- (6) C. M. Himel, R. T. Mayer, and L. L. Cook, *J. Polym. Sci., Part A-1*, **8**, 2219-2230 (1970).
- (7) S. K. Chakrabarti and W. R. Ware, *J. Chem. Phys.*, **55**, 5494 (1971).
- (8) L. Brand and J. R. Gohlke, *J. Biol. Chem.*, **246**, 2317 (1971).
- (9) C. J. Seliskar and L. Brand, *J. Am. Chem. Soc.*, **93**, 5414 (1971).
- (10) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1968).
- (11) C. J. Seliskar and L. Brand, *Science*, **171**, 799 (1971).
- (12) M. Godfrey and J. N. Murrell, *Proc. R. Soc. London, Ser. A*, **278**, 57 (1964); **278**, 64, 71 (1964).
- (13) C. J. Seliskar and L. Brand, *J. Am. Chem. Soc.*, **93**, 5405 (1971).
- (14) K. Nishimoto and R. Fujishiro, *Bull. Chem. Soc. Jpn.*, **37**, 1660 (1964).
- (15) K. Nishimoto, *Bull. Chem. Soc. Jpn.*, **39**, 645 (1966).
- (16) V. Fussgänger, *Ber.*, **35**, 976 (1902).
- (17) D. J. R. Laurence, *Methods Enzymol.*, **4**, 174 (1957).
- (18) R. F. Chen, *Nature (London)*, **209**, 69 (1966).
- (19) C. M. Himel and R. T. Mayer, *Anal. Chem.*, **42**, 130 (1970).
- (20) A. N. Fletcher, *J. Mol. Spectrosc.*, **23**, 22 (1967).
- (21) E. T. Mesewc, "Excited States of Proteins and Nucleic Acids", R. F. Steiner and I. Weinryb, Ed., Plenum Press, New York, N.Y., 1971, p 57.
- (22) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).
- (23) K. Dimroth, C. Reiehart, T. Siermann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).
- (24) E. M. Kosower and K. Tanizawa, *Chem. Phys. Lett.*, **16**, 419 (1972).
- (25) L. Stryer, *J. Am. Chem. Soc.*, **88**, 5708 (1966).
- (26) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).
- (27) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Wiley, New York, N.Y., 1963, Chapter 6.
- (28) M. Kasha and H. R. Rawls, *Photochem. Photobiol.*, **7**, 561 (1968).
- (29) N. Mataga, *Bull. Chem. Soc. Jpn.*, **36**, 654 (1963).
- (30) M. A. El-Bayonmi, J. P. Dalle, and M. F. O'Duyser, *J. Am. Chem. Soc.*, **92**, 3494 (1970).
- (31) S. G. Schulman and A. C. Capomacchia, *Spectrochim. Acta, Part A*, **28**, 1 (1972).
- (32) R. M. Hochstrasser and C. J. Marzocco in "Luminescence", E. C. Lim, Ed., W. A. Benjamin, New York, N.Y., 1969, pp 631-656.

Optically Active Amines. XVIII.¹ Spectral Observations on Optically Active N-Substituted Pyrroles

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Abstract: The CD spectra of (*R*)-1-(1,2,2-trimethylpropyl)pyrrole [(*R*)-**1**] and (*S*)-1-(1-phenylethyl)pyrrole [(*S*)-**2**] in hexane give evidence for the existence of a weak electronic transition of pyrrole between 230 and 240 nm which in the uv (isotropic absorption) spectrum is usually hidden under the tail of the more intense absorption band around 210 nm. The uv spectrum of (*R*)-**1** shows a maximum at 216 nm (ϵ 6400) and a shoulder near 202 nm (ϵ 4400). The CD spectrum displays a weak maximum at 236 nm ($[\theta]$ -670), a shoulder near 215 nm ($[\theta]$ -8300), and a strong maximum at 200 nm ($[\theta]$ -17,000). The Cotton effect at 236 nm is intensified by a phenyl substituent, and (*S*)-**2** shows a very intense maximum at 238 nm ($[\theta]$ +11,000). Based on the CD observations in conjunction with CNDO/S calculations, the 236- and 216-nm bands of the 1-pyrrolyl chromophore are assigned as $A_1 \leftarrow A_1$ and $B_2 \leftarrow A_1$ transitions of pyrrole, respectively, and the shoulder at 200 nm to the $B_1 \leftarrow A_1$ and $A_2 \leftarrow A_1$ transitions.

Until recently it was generally accepted that the uv (isotropic absorption) spectrum of pyrrole in hexane consists of a strong band in the vicinity of 210 nm (ϵ 5100) and a less distinct band near 240 nm (ϵ 300).⁴ However, it has been demonstrated with highly purified pyrrole that the long wavelength band in earlier measurements was the result of impurity.⁵ Our purpose now is to present evidence from the

CD spectra of chiral N-substituted pyrroles for the existence of a weak electronic transition of pyrrole between 230 and 240 nm⁶ which in the uv spectrum in hexane is usually hidden under the tail of the more intense band around 210 nm.⁷ On the basis of the CD observations in conjunction with CNDO/S calculations, we also assign this weak electronic transition as well as the other transitions responsible

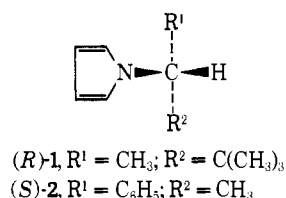
Table I. Parameters Used in CNDO/S Calculations

Atom	Slater exponent	Core integrals, eV		Repulsion integral, eV	Resonance integral, eV
		s	p		
C	1.625	28.10	11.14	11.11	-17.0
H	1.2	14.35	14.55	12.85	-12.0
N	1.95	38.63	14.55	12.01	-26.0

for the uv absorption of the 1-pyrrol chromophore between 200 and 300 nm. As we have noted in connection with the chiroptical properties of the pyridyl chromophore,⁸ this again demonstrates a useful feature of CD measurements in assisting in the location and the assignment of electronic transitions in uv spectra.

Results and Discussion

The uv and CD spectra of (*R*)-1-(1,2,2-trimethylpropyl)pyrrole [(*R*)-1] and (*S*)-1-(1-phenylethyl)pyrrole⁹ [(*S*)-2] in hexane are shown in Figure 1. Both (*R*)-1 and



(*S*)-2 were formed by condensation of (*R*)-2,2-dimethyl-3-aminobutane¹⁰ and (*S*)- α -phenylethylamine, respectively, with 2,5-dimethoxytetrahydrofuran in glacial acetic acid.⁹

The uv spectrum of (*R*)-1 shows a maximum at 216 nm (ϵ 6400) and a shoulder near 202 nm (ϵ 4400). The CD spectrum, on the other hand, displays a weak maximum at 236 nm ($[\theta]$ -670), a shoulder near 215 nm ($[\theta]$ -8300), and a strong maximum at 200 nm ($[\theta]$ -17,000). The Cotton effect at 236 nm is intensified by a phenyl substituent, and (*S*)-2 in hexane shows a very intense maximum at 238 nm ($[\theta]$ +11,000). The position of this Cotton effect is almost identical to the weak absorption band centered at about 237.5 nm observed in the vapor phase spectrum of pyrrole⁶ thus confirming the existence of a transition at this location.⁶ Indeed, calculations by Mullen and Orloff,⁶ using the CNDO/S method of Del Bene and Jaffe¹¹ with Mataga approximation for the electron repulsion integrals, have yielded the lowest energy transition in pyrrole to be A₁ \leftarrow A₁ with small oscillator strength. This transition is a $\pi \rightarrow \pi^*$ transition in which the excited electron is removed from a π orbital polarized toward the nitrogen atom.

In order to make assignments for the various uv bands, a knowledge of the nature of the Cotton effects corresponding to each electronic transition is extremely useful. To this end CNDO/S calculations for pyrrole were done using a more recent program,¹² modified to include the magnetic transition moment calculation.¹³ With the same geometry as used

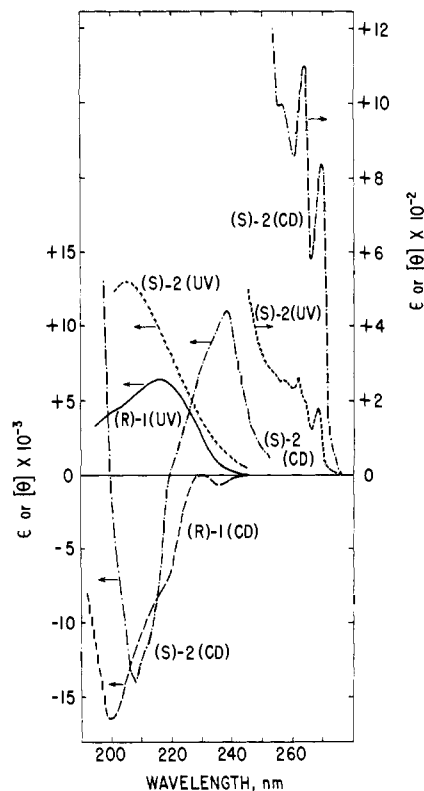


Figure 1. The uv and CD spectra of (*R*)-1-(1,2,2-trimethylpropyl)pyrrole [(*R*)-1] and (*S*)-1-(1-phenylethyl)pyrrole [(*S*)-2] in hexane.

by Mullen and Orloff⁶ and the parameters as summarized in Table I, the results obtained for the eight lowest energy excited states of pyrrole are shown in Table II. In addition to verifying the lowest energy transition to be 2A₁ \leftarrow 1A₁, it is also worth noting the emergence of the 1B₁ and 1A₂ states as the third and fourth excited states, respectively, in slight variance with the previous CNDO results.^{6,11} A recent INDO calculation on pyrrole¹⁴ also places these two states to be the third and fourth excited states with significant shift to lower energies. These results, also presented in Table II, are in good agreement with ours. It is more meaningful, however, to compare the uv spectrum of (*R*)-1 to that of *N*-methylpyrrole. The results of CNDO/S calculations on *N*-methylpyrrole are presented in Table III. It is significant that the lowest energy singlet $\pi \rightarrow \pi^*$ transition for *N*-methylpyrrole, as compared to pyrrole, is bathochromically shifted by 4.3 nm with an increase in oscillator strength.

Based on the transition energy and oscillator strength patterns of the SCF-MO calculations of pyrrole and *N*-methylpyrrole, we now assign the 236-nm transition of (*R*)-1, evident only in the CD spectrum, to the 2A₁ \leftarrow 1A₁ transition of pyrrole (Table II). Its weak isotropic absorp-

Table II. Eight Lowest Energy Excited States of Pyrrole

Symmetry ^a of excited state	Type	Transition wavelength, nm	Oscillator strength	Transition moment	
				Electric (μ), D	Magnetic (m), m _B
2A ₁	$\pi \rightarrow \pi^*$	226.7 (225.0) ^b	0.008 (0.004) ^b	0.603 (z)	
1B ₂	$\pi \rightarrow \pi^*$	224.8 (225.0)	0.288 (0.269)	3.701 (y)	0.423 (x)
1B ₁	$\pi \rightarrow \sigma^*$	177.1 (191.6)	0.000 (0.001)	0.018 (x)	0.218 (y)
1A ₂	$\pi \rightarrow \sigma^*$	176.8 (188.7)	0.000 ^c (0.0 ^c)		0.087 (z)
3A ₁	$\pi \rightarrow \pi^*$	171.7 (173.9)	0.952 (0.824)	5.890 (z)	
2B ₂	$\pi \rightarrow \pi^*$	170.6 (168.5)	0.202 (0.217)	2.703 (y)	0.250 (x)
2A ₂	$\pi \rightarrow \sigma^*$	163.5 (158.2)	0.000 ^c (0.0 ^c)		0.947 (z)
2B ₁	$\pi \rightarrow \sigma^*$	162.6 (153.7)	0.000 (0.002)	0.081 (x)	1.393 (y)

^a The z axis is the C₂ axis of pyrrole, and the yz plane is the ring plane. ^b Data in parentheses are from ref 14. ^c Forbidden.

Table III. Eight Lowest Energy Excited States of *N*-Methylpyrrole

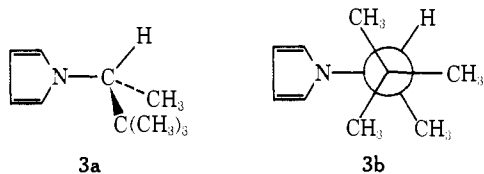
Symmetry ^a of excited state	Type	Transition wavelength, nm	Oscillator strength	Transition moment	
				Electric (μ), D	Magnetic (m), μ_B
2A'	$\pi \rightarrow \pi^*$	231.0	0.021	0.276 (y), 0.967 (z)	0.051 (x)
3A'	$\pi \rightarrow \pi^*$	224.5	0.277	3.631 (y), 0.022 (z)	0.443 (x)
1A''	$\pi \rightarrow \sigma^*$	176.8	0.001	0.151 (x)	0.208 (y), 0.001 (z)
2A''	$\pi \rightarrow \sigma^*$	175.7	0.000	0.003 (x)	0.000 (y), 0.006 (z)
4A'	$\pi \rightarrow \pi^*$	175.6	0.916	0.247 (y), 5.840 (z)	0.021 (x)
5A'	$\pi \rightarrow \pi^*$	174.7	0.266	3.130 (y), 0.298 (z)	0.059 (x)
3A''	$\pi \rightarrow \sigma^*$	163.6	0.000	0.028 (x)	0.326 (y), 0.805 (z)
4A''	$\pi \rightarrow \sigma^*$	162.4	0.000	0.020 (x)	1.391 (y), 0.213 (z)

^aThe conformation of *N*-methylpyrrole is such that a methyl hydrogen atom eclipses the pyrrol ring plane which is also the *yz* plane. Consequently, the symmetry of the point group is C_s .

tion is hidden under the strong band centered around 216 nm which is assigned to the $1B_2 \leftarrow 1A_1$ transition. The shoulder at 200 nm in the uv spectrum of (*R*)-**1** is due to the $1B_1 \leftarrow 1A_1$ and $1A_2 \leftarrow 1A_1$ transitions. Interpretation of the observed CD spectra of both (*R*)-**1** and (*S*)-**2** supports these assignments.

Three important mechanisms which account for the generation of Cotton effects are well known:¹⁵ the one-electron, the coupled oscillator, and the electric (μ_1)-magnetic (m_2) coupling mechanisms. In the one-electron mechanism, sometimes referred to as static coupling, it is the static field of the perturbant which causes the mixing of the excited states of the chromophore resulting in parallel components of the electric and magnetic transition moments. The other two mechanisms are sometimes termed dynamic coupling¹⁶ since it is the electric or magnetic transition moment of the perturbant which interacts with the electric or magnetic transition moment of the chromophore. When the perturbant and chromophore transitions occur in close energetic proximity, dynamic coupling will be dominant, but when they are energetically far apart, such as an alkyl group acting as perturbant on an aromatic chromophore, static coupling can become more important.

In (*R*)-**1**, a negligible contribution by the coupled oscillator mechanism is anticipated for the $2A_1 \leftarrow 1A_1$ transition since in the preferred conformation of (*R*)-**1** (**3** in two views **3a** and **3b**)¹⁷ the methyl and *tert*-butyl groups are symmet-



rically disposed with respect to the symmetric axis of the pyrrol ring on which the electric transition moment of the $2A_1 \leftarrow 1A_1$ transition lies. The dipolar contribution to the rotational strength through the interaction of this transition moment with the bond transition moments of the chiral carbon-methyl group bond and the chiral carbon-*tert*-butyl group bond will not produce Cotton effects since they merge to the same carbon atom (**3a**). Since the three methyl groups of the *tert*-butyl group are also symmetrically oriented with respect to the $2A_1 \leftarrow 1A_1$ electric transition moment (**3b**), their contribution to the rotational strength will also sum to zero. Any effect due to the carbon-hydrogen bonds can be neglected since their polarizabilities are quite small compared to that of a carbon-carbon bond,¹⁸ and their effects tend to cancel each other. For the $1B_2 \leftarrow 1A_1$ transition, the electric transition moment is perpendicular to the attachment bond. Thus interactions with the bond moments of all of the carbon-carbon bonds must be included in the coupled oscillator calculation.¹⁹ Using the geometry of the preferred conformation **3**, the calculation gives a

rotational strength which is opposite in sign to the observed Cotton effect for the 215-nm band. Thus we must assume that the observed Cotton effects arise primarily from the one-electron mechanism.

According to the one-electron mechanism,²⁰ an electronic transition in a symmetric chromophore can acquire a Cotton effect by dissymmetric perturbation only through the mixing with those excited states of the chromophore which have magnetic (or electric) transition moments parallel to the electric (or magnetic) transition moment of that particular transition. The sign and magnitude of the induced Cotton effect depend on the magnitudes and directions of those transition moments as well as the coefficient of mixing. The coefficient of mixing in turn is directly proportional to the extent of the chromophore-perturbant interaction and inversely proportional to the energy separation of these two mixed states.

The evaluation of the matrix elements of the perturbing potential is rather involved. Thus, in what follows, the CD spectrum of (*R*)-**1** will be interpreted qualitatively in terms of the magnitudes of the relevant electric and magnetic transition moments as well as the energy separation which we assume to outweigh the variation in perturbing potential. Direct CNDO/S calculations of optical activity were not made because of a special parameter used which makes the calculation suitable only for planar or nearly planar molecules.²¹

Since the preferred conformation of (*R*)-**1** is such that the hydrogen atom at the chiral center eclipses the pyrrol ring plane (**3a**),¹⁷ the optical activity of (*R*)-**1** can be regarded as arising essentially from the asymmetric substitution of *N*-methylpyrrole with a methyl hydrogen atom eclipsing the pyrrol ring plane. The analysis should then be done using Table III. However, since the qualitative interpretations do not differ greatly, we prefer to deal with the pyrrole chromophore (Table II) for the sake of simplicity.

If we assume the optical activity of (*R*)-**1** to arise by the one-electron mechanism from the dissymmetric substitution of pyrrole, it can readily be seen from Table II or a group character table of the C_{2v} symmetry point group that in order to produce Cotton effects, the A_1 states of pyrrole must mix with the A_2 states, and the B_1 states with B_2 states. Considering only the first eight excited states of pyrrole, the Cotton effect associated with the $2A_1 \leftarrow 1A_1$ transition can be seen to arise from the admixture of the $2A_1$ with the $1A_2$ and $2A_2$ states. The $2A_2$ state appears to give a larger contribution because of its larger magnetic transition moment (m_y). As is observed for the 236-nm band of (*R*)-**1**, the Cotton effect for the $2A_1 \leftarrow 1A_1$ transition, however, is not expected to be large because of its small electric transition moment (μ_z) as well as the unfavorable energy factor.

The Cotton effect for the $1B_2 \leftarrow 1A_1$ transition results from the admixture of the $1B_2$ with the $1B_1$ and $2B_1$ states which generate a magnetic transition moment along the *y*

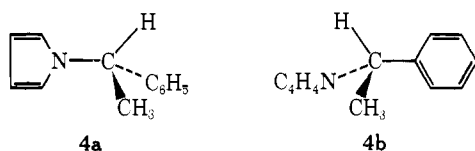
axis and an electric transition moment along the x axis of the chromophore. The large electric transition moment (μ_y) of the $1B_2 \leftarrow 1A_1$ transition combined with the large magnetic transition moment (m_y) of the $2B_1 \leftarrow 1A_1$ transition will result in a sizable Cotton effect although the energy factor will reduce its magnitude somewhat. The band near 216 nm which has a large maximum in the uv spectrum and a shoulder in the CD spectrum appears to conform to the predicted behavior of the $1B_2 \leftarrow 1A_1$ transition.

For the $1A_2 \leftarrow 1A_1$ transition, the admixture of the $1A_2$ state with the $2A_1$ and $3A_1$ states produces a nonvanishing electric transition moment component along the symmetric z axis. The mixing with the $3A_1$ state will be the dominant factor because of the large oscillator strength for the $3A_1 \leftarrow 1A_1$ transition and the very small energy separation between the $1A_2$ and $3A_1$ states. Thus, a strong Cotton effect is to be expected. Similarly, a large Cotton effect is also expected for the $1B_1 \leftarrow 1A_1$ transition through admixture with the $1B_2$ and $2B_2$ states. These predictions are readily borne out by the 200-nm band of (*R*)-**1** which shows only a shoulder in the isotropic absorption spectrum but an unusually large CD maximum. The magnetic nature of this band can readily be seen from its large optic anisotropy, $\Delta\epsilon/\epsilon$.

The uv spectrum of (*S*)-**2** (Figure 1) consists of a weak absorption band with vibrational fine structure centered around 265 nm and a strong band at 205 nm. The former is characteristic of the $1B_{2u} \leftarrow 1A_{1g}$ transition and the latter the $1B_{1u} \leftarrow 1A_{1g}$ transition of the benzene chromophore. The corresponding CD spectrum shows weak positive $1B_{2u} \leftarrow 1A_{1g}$ maxima centered at about 265 nm, a strong positive Cotton effect at 238 nm, a negative maximum at 208 nm, and strong positive dichroic absorption below 200 nm.

The analysis of the CD spectrum of (*R*)-**1** suggests that the Cotton effect at 238 nm in the CD spectrum of (*S*)-**2** is the enhancement of the 236-nm band in (*R*)-**1** as a result of dipolar interaction of pyrrole $2A_1 \leftarrow 1A_1$ transition with the transverse component of the $1E_{1u} \leftarrow 1A_{1g}$ transition in benzene. The CD maximum at 208 nm corresponds to the $1B_{1u} \leftarrow 1A_{1g}$ transition of the benzene chromophore and the steep rising Cotton effect below 200 nm to the $1B_1 \leftarrow 1A_1$ and $1A_2 \leftarrow 1A_1$ transitions of pyrrole. The latter results from the interaction between the magnetic transition moments of these transitions with the electric transition moments of the $1B_{1u} \leftarrow 1A_{1g}$ transition and possibly the $1E_{1u} \leftarrow 1A_{1g}$ transition of benzene as well as the one-electron mechanism.

To verify the assignment of the 238-nm maximum to the $2A_1 \leftarrow 1A_1$ transition of pyrrole, a calculation of the contribution to the rotational strength due to the coupled oscillator mechanism was done. The preferred conformation of (*S*)-**2** is taken to be that with the hydrogen atom at the chiral center eclipsing both the pyrrol and phenyl ring planes (**4** in two views **4a** and **4b**).^{17,22} The rotational



strength (R) due to a coupled oscillator is given by

$$R_1 = \frac{2\pi}{hc} \frac{\nu_1 \nu_2}{(\nu_2^2 - \nu_1^2)} \left[\frac{\mu_1 \cdot \mu_2}{R_{12}^3} - \frac{3(\mu_1 \cdot \mathbf{R}_{12})(\mu_2 \cdot \mathbf{R}_{12})}{R_{12}^5} \right] \times \mu_1 \times \mu_2 \cdot \mathbf{R}_{12} \quad (1)$$

where the subscript 1 refers to the transition of interest and subscript 2 to the perturbant transition, μ and ν are electric transition moments and the transition frequency, respectively, and $\mathbf{R}_{12} = \mathbf{R}_2 - \mathbf{R}_1$.

The electric transition moment of the $2A_1 \leftarrow 1A_1$ transition of pyrrole can interact with the transition moments of the $1B_{2u} \leftarrow 1A_{1g}$ and $1B_{1u} \leftarrow 1A_{1g}$ as well as the $1E_{1u} \leftarrow 1A_{1g}$ transitions of benzene. The effect of the $1B_{2u} \leftarrow 1A_{1g}$ transition will be small because of its weak isotropic absorption. The electric transition moment of the $1B_{1u} \leftarrow 1A_{1g}$ transition and the longitudinal component of the $1E_{1u} \leftarrow 1A_{1g}$ transition both lie along the attachment bond of the phenyl ring while the electric transition moment of the $2A_1 \leftarrow 1A_1$ transition lies along the attachment bond of the pyrrol ring. Since both attachment bonds meet at the same carbon atom, the $\mu_1 \times \mu_2 \cdot \mathbf{R}_{12}$ factor in (1) will be zero thus giving no contribution to the rotational strength of the $2A_1 \leftarrow 1A_1$ transition. Consequently, the only contribution to the rotational strength can come from interaction between the $2A_1 \leftarrow 1A_1$ transition of pyrrole and the transverse component of the $1E_{1u} \leftarrow 1A_{1g}$ transition of benzene. The electric transition moment of the $2A_1 \leftarrow 1A_1$ transition of pyrrole (μ_2) and the transverse component of the $1E_{1u} \leftarrow 1A_{1g}$ transition of benzene were found by CNDO/S calculations on *N*-methylpyrrole and toluene to be about 1 (Table III) and 10 D, respectively. With the point dipole approximation and placing the transition moments at the center of the respective rings, the rotational strength for the 238-nm band of (*S*)-**2** was calculated using (1) to be $+3 \times 10^{-40}$ cgs units. This is to be compared with the experimental rotational strength of $+5 \times 10^{-40}$ cgs units estimated from Figure 1.²³

Experimental Section

Boiling points are not corrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Uv spectra were measured with a Cary Model 14 spectrophotometer using 1-cm sample cells and the normal variable slit. CD spectra were measured in hexane at 25–28° with a Cary Model 60 spectrophotometer with a CD Model 6001 accessory. The slit was programmed for a spectral band width of 1.5 nm, and a 0.1-mm cell was used.

Preparation of *N*-Substituted Pyrroles. The primary amine was boiled with an approximately 2% molar excess of 2,5-dimethoxytetrahydrofuran in glacial acetic acid (0.25 ml/mmol amine) for 2 hr. For purification of the product, the best method is different from that reported.⁹ The acetic acid was neutralized with 25% aqueous potassium hydroxide and an additional amount of 25% aqueous potassium hydroxide was added (1 ml/mmol amine). This mixture was boiled for 3 hr to hydrolyze any *N*-substituted acetamide formed in the initial reaction. The cooled solution was extracted with ether, and the ether solution was washed with water. The ether solution was then saturated with carbon dioxide. Any unreacted amine was thus precipitated as its carbamate salt. The latter was removed by filtration. The ether solution was dried (MgSO_4) and evaporated. The residual oil was distilled.

(*R*)-1-(1,2,2-trimethylpropyl)pyrrole [(*R*)-1**]** was prepared in 57% yield from (*R*)-2,2-dimethyl-3-aminobutane, $[\alpha]^{24D} +5.4^\circ$ (neat) [lit.¹⁰ $[\alpha]^{24D} +5.4^\circ$ (neat)]. (*R*)-**1**: bp 84–85° (25 mm); n_D^{25} 1.4752; d_4^{20} 0.874; $[\alpha]^{24D} -27.1^\circ$ (*c* 8.55, CH_3OH); and CD (*c* 1.63) $[\theta]_{325} \pm 0$, $[\theta]_{245} \pm 0$, $[\theta]_{236} -670$ (max), $[\theta]_{232} \pm 0$ and (*c* 0.195) $[\theta]_{230} \pm 0$, $[\theta]_{215} -8300$ (shoulder), $[\theta]_{200} -17,000$ (max), $[\theta]_{192} -7800$.

Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{N}$: C, 79.40; H, 11.34; N, 9.26. Found: C, 79.39; H, 11.31; N, 9.30.

(*S*)-1-(1-phenylethyl)pyrrole [(*S*)-2**]** was prepared in 51% yield from (*S*)- α -phenylethylamine, $[\alpha]^{23D} -40.7^\circ$ (neat) [lit.²⁴ $[\alpha]^{23D} +39.9^\circ$ (neat) for the (*R*) isomer]. (*S*)-**2**: bp 106–108° (3 mm); n_D^{25} 1.5589; d_4^{20} 1.003; $[\alpha]^{25D} +46^\circ$ (*c* 0.94, absolute $\text{C}_2\text{H}_5\text{OH}$); $[\alpha]^{24D} +50.4^\circ$ (neat) [lit.⁹ $[\alpha]^{25D} +47.65^\circ$ (neat), 93.3% optically pure]; and CD (*c* 3.27) $[\theta]_{325} \pm 0$, $[\theta]_{277} \pm 0$, $[\theta]_{269} +850$ (max), $[\theta]_{266} +580$ (min), $[\theta]_{263} +1100$ (max), $[\theta]_{260} +860$ (min), $[\theta]_{256} +1000$ (max), $[\theta]_{255} +990$ (min), $[\theta]_{250} +2100$ and (*c* 0.327) $[\theta]_{250} +1800$, $[\theta]_{238} +11,000$ (max), $[\theta]_{230} +7800$, and (*c* 0.0654) $[\theta]_{230} +9000$, $[\theta]_{219} \pm 0$, $[\theta]_{208} -14,000$ (max), $[\theta]_{200} \pm 0$, $[\theta]_{198} +13,000$.

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References and Notes

- (1) Paper XVII: H. E. Smith, A. W. Gordon, and A. F. Bridges, *J. Org. Chem.*, **39**, 2309 (1974).
- (2) (a) Vanderbilt University; (b) Tennessee State University.
- (3) National Science Foundation Undergraduate Summer Fellow, 1973.
- (4) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products", Pergamon Press, New York, N.Y., 1964, pp 165 and 166.
- (5) G. Horvath and A. I. Kiss, *Spectrochim. Acta, Part A*, **23**, 921 (1967).
- (6) P. A. Mullen and M. K. Orloff, *J. Chem. Phys.*, **51**, 2276 (1969).
- (7) "UV Atlas of Organic Compounds", Vol. V, Plenum Press, New York, N.Y., 1971, G1/4.
- (8) H. E. Smith, L. J. Schaad, R. B. Banks, C. J. Wiant, and C. F. Jordan, *J. Am. Chem. Soc.*, **95**, 811 (1973).
- (9) J. M. Patterson, L. T. Burka, and M. R. Boyd, *J. Org. Chem.*, **33**, 4033 (1968).
- (10) H. E. Smith and H. E. Ensley, *Can. J. Chem.*, **49**, 2902 (1971).
- (11) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 4050 (1968).
- (12) J. Del Bene, H. H. Jaffe, R. L. Ellis, and G. Kuehnlenz, "CNDO/S-CI Molecular Orbital Calculations with the Complete Neglect of Differential Overlap and Configuration Interaction", Program 174, Quantum Chemistry Program Exchange (QCPE), Indiana University, Bloomington, Ind.
- (13) Magnetic transition moments were calculated according to the method described by J. Linderberg and J. Michl, *J. Am. Chem. Soc.*, **92**, 2619 (1970).
- (14) J. Ridley and M. Zerner, *Theor. Chim. Acta*, **32**, 111 (1973).
- (15) J. A. Schellman, *Acc. Chem. Res.*, **1**, 144 (1968).
- (16) E. G. Hohn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).
- (17) G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).
- (18) W. H. Inskip, D. W. Miles, and H. Eyring, *J. Am. Chem. Soc.*, **92**, 3866 (1970).
- (19) Details of the coupled oscillator calculation with transition bond moment approximations can be found in ref 18.
- (20) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).
- (21) J. N. Murrell and A. J. Harget, "Semi-empirical self-consistent-field molecular orbital theory of molecules", Wiley-Interscience, New York, N.Y., 1972, p 46.
- (22) P. Salvadori, L. Lardicci, R. Menicagli, and C. Bertucci, *J. Am. Chem. Soc.*, **94**, 8598 (1972).
- (23) C. Djerassi, "Optical Rotatory Dispersion", McGraw-Hill, New York, N.Y., 1960, pp 164-167.
- (24) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

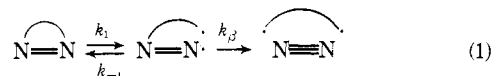
High Pressure Studies. XVII. Thermal Decomposition of Cyclic Azo Compounds^{1,2}

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Abstract: The effects of pressure on the decomposition of the cyclic azo compounds, *cis*-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (**1**), *cis*-3,7-diphenyl-1,2-diaza-1-cycloheptene (**2**), and *cis*-3,8-diphenyl-*cis*-1,2-diaza-1-cyclooctene (**3**), have been investigated in toluene at 60 or 65°. Kinetic studies give decomposition activation volumes for **1** and **2** of ca. +5.5 cm³/mol, while that for **3** is +7.1 cm³/mol. Product studies from 1 to 5000 atm show that the ratio of styrene to 1,2-diphenylcyclobutane from **1** decreased from 1.4 to 1.1, while the ratio of *cis*- to *trans*-1,2-diphenylcyclobutane increased from 2.5 to 4.6. The ratio of 1,5-diphenyl-1-pentene to 1,2-diphenylcyclopentane from **2** increased from 0.2 to 0.4, while the ratio of *cis*- to *trans*-1,2-diphenylcyclopentane increased slightly from 1.1 to 1.2. The ratio of 1,6-diphenyl-1-hexene to 1,2-diphenylcyclohexane products from **3** increased from 0.9 to 1.3, but the *cis*- to *trans*-1,2-diphenylcyclohexane ratio *decreased* from 1.0 to 0.6. The results are interpreted in terms of simultaneous two-bond scission of **1** and **2** to give the intermediate carbon diradicals as primary products. The data for **3** suggest one-bond C-N scission with the formation of a diazenyl diradical as the first diradical intermediate.

One mechanism for decomposition of cyclic azo compounds might be one-bond scission to give an unstable diradical (k_1) which could lose nitrogen (k_β) in competition with reclosure (k_{-1}) (eq 1).^{4,5} If this occurred, we thought



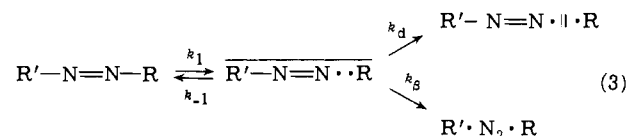
that it might be kinetically detectable by the effect of pressure on the decomposition rates.⁶ The apparent activation volume for decomposition (eq 2) would depend not only on

$$\Delta V^*_{\text{obsd}} = \Delta V_1^* + RT \partial \ln (1 + k_{-1}/k_\beta) / \partial P \quad (2)$$

that for the homolysis step (ΔV_1^*) but also on the pressure dependence of the competition between closure (k_{-1}) and β scission (k_β). Since that ratio might be expected to increase with increasing pressure [radical combination and homolytic scission (k_β) being accelerated and retarded, respectively, by pressure],⁶ values of ΔV^*_{obsd} for such cyclic azo compounds would be larger than those for cyclic systems where concerted loss of nitrogen led directly to the final diradical shown in eq 1.

A basis for these assumptions is found in our observations

that activation volumes for decomposition of *acyclic* azo compounds are relatively small and constant when nitrogen is lost concertedly and much larger for a series of phenylazotriphenylmethanes ($\text{PhN}=\text{NCPh}_3$) which decompose via initial scission of just the N-CPh₃ bond (Table I).⁷ However, it is likely that a substantial part of this difference for acyclic systems is due to a high-pressure effect on separative diffusion (k_d , eq 3).^{6,8,9} The observed activation volume



for acyclic systems (eq 4) differs from that for cyclic sys-

$$\Delta V^*_{\text{obsd}} = \Delta V_1^* + RT \partial \ln [1 + k_{-1}/(k_\beta + k_d)] / \partial P \quad (4)$$

tems (eq 2) by the inclusion of the rate constant k_d in the differential term. Since pressure retardation of k_d is much greater than any effect on k_β , it is conceivable that the differential term in eq 4 is substantially greater than the analogous term in eq 2.