Table I. Second-Order Rate Constants k_2 for the Reduction and Yields of 2-Pyridylmethanol (**4**)[a]

	dihydroquinoline	
$[ZnCl_2]$, M	**2a** (yield of **4**, %)	**2b** (yield of **4**, %)
0	<0.3 (<5)[d] <0.3[b]	<0.3 (<5)[d]
0.01	1.2 ± 0.1 (65)[d]	1.7 ± 0.2 (88)[d]
0.1	8.4 ± 0.9 (95)[d] 18.7 ± 0.4[b] 17.0 ± 1.4[c]	13.1 ± 0.7 (93)[d]
0.5	26.4 ± 1.3	
1.0	58.7 ± 8.3 (98)[e]	72.1 + 11.5 (96)[e]

[a] pH 4.7, 50 °C, h^{-1} M^{-1}, $k_2 = (k_{obsd} - k_o)/[\mathbf{3}]$ where k_o is the spontaneous decrease of **2**. Errors are standard deviations. [b] NaCl (1 M) was added. [c] $NaClO_4$ (1 M) was added. [d] Yields after 30 h. [e] Yield after 15 h.

determined by HPLC using pyridine as an internal standard, being good to excellent depending on the Zn^{2+} concentration (see Table I).

The rate constants[12] corrected for the spontaneous decrease of **2** (vide infra) and the yield of **4** are summarized in Table I (see also Figure 1). It should be reemphasized that the rates and yields were reproducible only when oxygen was carefully removed and the reaction was carried out in the dark. The amount of recovered quinolinium salt **1** after the reaction determined by HPLC was higher than 95%.

Obviously, Table I shows that the yields were much improved and the rates were remarkably accelerated by the increase of Zn^{2+} concentration contrary to the previous observations.[13] Rates were further accelerated to some extent by the addition of 1 M NaCl or $NaClO_4$ (see Table I), demonstrating the existence of a moderate salt effect.

The following kinetic and spectroscopic observations were made:

(i) Plot of k_2 against $[Zn^{2+}]$ showed the gradual rate saturation at higher Zn^{2+} concentration.

(ii) Linear correlations were observed between $1/k_{obsd}$ and $1/[Zn^{2+}]$ [3] (Figure 1). The equilibrium constant K_2 and the rate constant k_2 (Scheme I) estimated from the dependence of rate on the concentration of 3 and Zn^{2+} were (58 ± 16) M^{-2} and (1.3 ± 0.3) h^{-1}, respectively, at 1.0 M $ZnCl_2$.

Scheme I

$$\mathbf{3} + Zn^{2+} \underset{}{\overset{K_1}{\rightleftarrows}} \mathbf{3}\cdot Zn^{2+}$$

$$\mathbf{2} + \mathbf{3} + Zn^{2} + \overset{K_2}{\rightleftarrows} \mathbf{2}\cdot\mathbf{3}\cdot Zn^{2+}$$

$$\mathbf{3}\cdot Zn^{2+} + \mathbf{2} \xrightarrow[\text{rds}]{k_1} \mathbf{1} + \mathbf{4} + Zn^{2+}$$

$$\mathbf{2}\cdot\mathbf{3}\cdot Zn^{2+} \xrightarrow[\text{rds}]{k_2} \mathbf{1} + \mathbf{4} + Zn^{2+}$$

(iii) The maxima of fluorescence spectra of **2a** and **2b** were shifted to longer wavelength and intensities markedly decreased by the addition of Zn^{2+} and **3**, but they were not shifted by the addition of **3** alone. These observations indicate ternary complex formation.

On the basis of these observations a conclusion is drawn that the reduction of **3** with **2** proceeds mainly through a ternary complex, $\mathbf{2}\cdot\mathbf{3}\cdot Zn^{2+}$.

By comparison of the rate of **2a** with **2b** (Table I), introduction of a hydroxyl group in dihydroquinoline appreciably accelerates the rates[9] in the presence of Zn^{2+} (0.01 to ~ 1.0 M). The acceleration suggests the enhanced interaction promoted by additional coordination between OH and Zn^{2+}.

Reduction of **3** with **2** was remarkably affected by O_2 and light,[14] and both reactions were independently affected by Zn^{2+}, making the kinetic situation very complicated. Dioxygen lead to nonproductive consumption of **2** (oxidation to **1** by O_2) and irradiation with Xe lamp (>390 nm, 500 W) or even room light accelerated the rate of decrease of **2** considerably. The photochemistry will be discussed in detail in a forthcoming article.

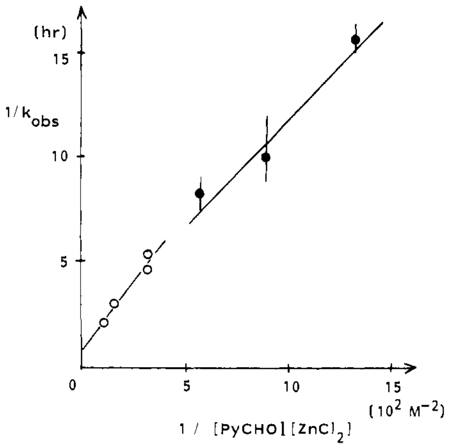

Figure 1. Plot of k_{obsd} vs. $1/[\mathbf{3}][ZnCl_2]$. Two lines drawn are the least-mean-square fit for each set of different ionic strength: $[ZnCl_2]$, 1.0 M (○); $[ZnCl_2]$, 0.1 M (●).

Registry No. 2a, 20224-92-4; **2b**, 84811-86-9; **3**, 1121-60-4; $ZnCl_2$, 7646-85-7.

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(12) Rates of spontaneous decrease is from 2% to 10% of k_{obsd}.

(13) Inhibition by metal ions was reported in a similar system,[7] without mentioning the effect of O_2 and light. The previous work[7] may not pay satisfactory attention to these.

(14) For the effect of light, see; Fukuzumi, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1983**, *105*, 4722 and references therein. However, for carbonyl reduction, a sole example is known for intramoleculr reaction: Sammes, J. D.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1023.

Vibrational Circular Dichroism of α-Phenylethylamine

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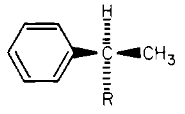
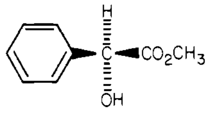
α-Phenylethylamine (**1**) has drawn considerable attention in the relatively new area of vibrational optical activity (VOA),[1,2]



(*R*)-1, R = NH_2
(*R*)-2, R = OH
(*R*)-3, R = N=C=O



(*S*)-4

due, in part, to the possible role of the methyl group as a probe for the assignment of absolute configuration. The infrared vibrational circular dichroism (VCD) spectrum in the 3500–2700-cm^{-1} region[3] and in the 1480–1400-cm^{-1} region[4] has been reported. Now we report the mid-infrared VCD spectrum in the 1625–900-cm^{-1} range with three objectives: first, to report an unusual pattern of VCD features, second, to show that the VCD associated with C*–H and the phenyl ring vibrational modes appear to be significant in understanding the relation of VCD

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(1) Hug, W.; Kint, S.; Bailey, G. F.; Scherer, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 5589–5590.

(2) Barron, D. *Nature (London)* **1975**, *255*, 458–460.

(3) Nafie, L. A.; Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 2715–2723.

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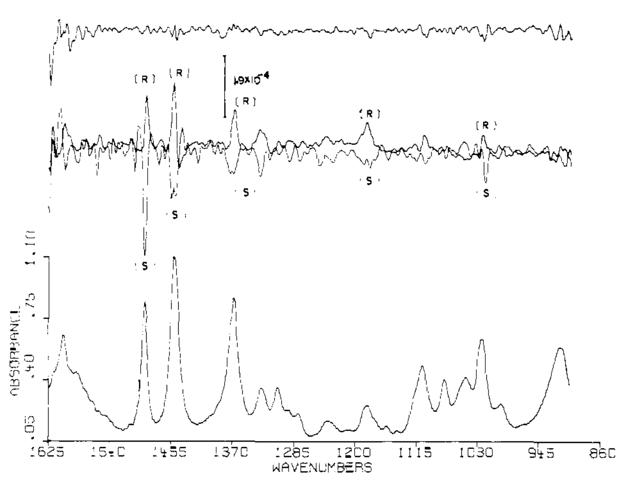

Figure 1. VCD spectra for both enantiomers of α-phenylethylamine. The bottom trace is the absorption spectrum and the middle traces are the CD spectra, in difference absorbance units, with labels R and S representing the enantiomers. Each CD spectrum is obtained from 12000 AC scans and 192 DC scans. The topmost trace represents the difference between the CD obtained from the first and last halves of the data collected and represents the level of spectral reproducibility.

features to stereochemistry, and finally, to show that the mid-infrared VCD of α-phenylethylamine as a neat liquid differs from that as a dilute solution in carbon tetrachloride.[4]

The VCD measurements reported here were done with a Fourier transform infrared spectrometer described elsewhere.[5,6] Samples of racemic and (R)- and (S)-α-phenylethylamine were freshly distilled under nitrogen[7] and were studied as the neat liquids in a variable path length cell. Spectral artifacts were nullified by subtracting the raw VCD spectrum of the racemate from those of the enantiomers. The VCD spectra for both (R)-**1** and (S)-**1** are overlayed in Figure 1 where their mirror image quality can be seen to be quite satisfactory with positive VCD bands being associated with (R)-**1** and negative ones with (S)-**1**. The basic features of these spectra are found to be reproducible in different runs.

In the C–H stretching region[3] of (S)-**1** a negative VCD band at 2961 cm^{-1} (partially shown in Figure 2b of ref 3) appears reasonably balanced with a positive VCD band at 2864 cm^{-1}. As seen in Figure 1, in the 1625–900-cm^{-1} region, however, there are seven VCD bands located at 1493, 1452, 1368, 1330, 1182, 1107, and 1024 cm^{-1} all with the same sign. This is unprecedented since no other molecule has yet been found to have this type of VCD pattern in such a wide spectral region. The implication of this observation may be conceived as follows. According to Faulkner,[9] in a fixed partial charge concept the sum of the rotational strengths for all $(3N - 6)$ vibrational bands of a chiral molecule should sum to zero. The nature of high- and low-frequency vibrational motions permits the application of this statement separately for the rotational strength of high-frequency motions such as C–H, N–H, and O–H stretching modes and low-frequency motions, such as the modes appearing in the mid infrared and toward the far infrared. The experimentally found balance between positive and negative features in the C–H stretching region, for example, of (R)-3-methylcyclohexanone,[10–12] supports this viewpoint. If the approximate sum rule[9] should hold, then one would expect to see measurable VCD bands in the 900–100-cm^{-1} region with signs opposite to those seen in Figure 1. In the 900–600-cm^{-1} region, there are three strong absorption bands, but our attempts to find measurable VCD associated with these bands were not successful. For the bands below 600 cm^{-1}, VCD is then expected to be measurable and hence the associated dissymmetry factors should be comparable to those seen in Figure 1 and in Figure 2b of ref 3. This is equivalent to saying that the rotational strengths for the bands below 600 cm^{-1} are expected to be larger than those measured for higher frequency bands. This observation contradicts the earlier prediction of equal rotational strengths[13] for high- and low-frequency vibrations. Nevertheless, it would be valuable to measure VCD in the as yet inaccessible region, namely, below 600 cm^{-1}, to verify the practical utility of the approximate sum rule.[9]

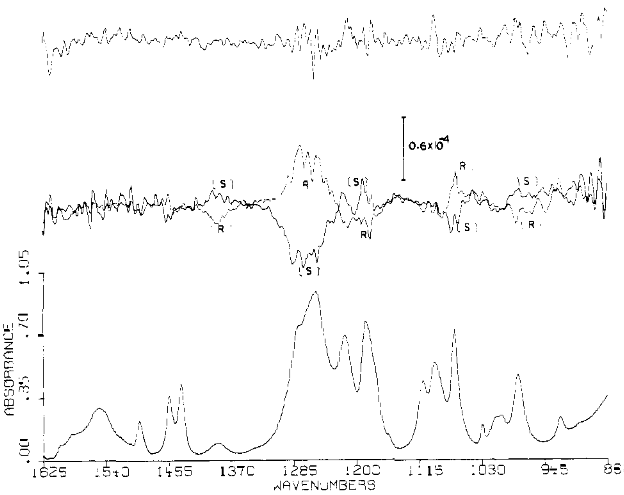

Figure 2. VCD spectra for both enantiomers of methyl mandelate measured as 0.4 M carbon tetrachloride solutions. For other details see the legend to Figure 1.

The bands at 1368 and 1182 cm^{-1} in α-phenylethylamine appear to have significance in relating VCD to stereochemistry. These bands are most likely due to the deformation modes of C*–H and the C–H bonds in the benzene ring. We have also found corresponding positive VCD bands as in Figure 1 for (R)-α-phenylethyl alcohol[14] [(R)-**2**] at 1368 and 1204 cm^{-1}, for (R)-α-phenylethyl isocyanate[15] [(R)-**3**] at 1205 cm^{-1}, and for methyl (S)-mandelate[16] [(S)-**4**] at 1388 and 1216 or 1188 cm^{-1}. For a better comparison, the VCD spectra of (S)-**4** and (R)-**4** are shown in Figure 2.

The consistant positive sign for the VCD bands near 1370 and 1200 cm^{-1} for (R)-**1**–**3** and (S)-**4** suggests that the main VCD contribution to these modes may be from the φ-C*–H moiety. Since in the most preferred conformation the plane of the benzene ring is almost orthogonal to the C*–C bond in **1**–**4**,[18,19] one can expect significant magnetic dipole transition moment contribution from the charge flow in the benzene ring during C*–H bond deformation. Thus if the φ-C*–H moiety is the source of these

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(6) Polavarapu, P. L.; Michalska, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 6190–6191.

(7) (R)- and (S)-α-phenylethylamine had $[\alpha]^{26}_{D}$ +23° (c 2.01, CH_3OH) and −27° (c 2.00, CH_3OH), respectively. Comparison of these rotatory powers with that given in ref 8 for (S)-**1** [$[\alpha]^{20}_{D}$ −28° (c 2, CH_3OH)] with 99% enantiomeric excess (ee), determined by the ^1H NMR method of Jacobus, Rabin, and Mislow, gives for our samples of (R)-**1** and (S)-**1** 81% and 95% ee, respectively.

(8) Gottarelli, G.; Samori, B. *J. Chem. Soc. B* **1971**, 2418–2423.

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(13) Barron, L. D. In "Optical Activity and Chiral Discrimination"; Mason, S. F., Ed.; Reidel: Boston, 1979; pp 249–250.

(14) $[\alpha]^{25}_{D}$ +39° (neat).

(15) Obtained from Aldrich Chemical Co. and used without further purification. $[\alpha]^{19}_{D}$ +9.6° (neat) is the quoted optical rotation.

(16) (R)- and (S)-methyl mandelate had $[\alpha]^{23}_{D}$ −169° (c 1.56, $CHCl_3$) and $[\alpha]^{23}_{D}$ +166° (c 1.42, $CHCl_3$), respectively. Comparison of these values with the maximum value reported, $[\alpha]^{20}_{D}$ −177° (c 1.3, $CHCl_3$), for (R)-**4** in ref 17 gives for our samples of (R)-**4** and (S)-**4** 95% and 94% ee, respectively.

(17) Arpesella, L.; La Manna, A.; Grassi, M. *Gazz. Chim. Ital.* **1955**, *85*, 1354–1364.

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VCD bands then the sign of these modes may be useful to fix the absolute configurations of approximately substituted analogues.

As a final note the mid-infrared VCD of (*R*)-α-phenylethylamine differs from that obtained as a dilute solution in carbon tetrachloride. The band at 1425 cm^{-1} (Figure 1) has positive VCD for (*R*)-**1**, which in carbon tetrachloride was reported[4] to be negative. This difference may be due to a product from the free radical reaction of the amine with carbon tetrachloride,[20] which quickly yields a number of products as well as a white precipitate.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-29375 and HD-05797) and the Vanderbilt University Research Council.

Registry No. (*R*)-**1**, 3886-69-9; (*S*)-**1**, 2627-86-3.

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Remarkable Disruption of a Porphyrin. Insertion of a Ruthenium Atom into a Pyrrole Carbon–Nitrogen Bond of an *N*,*N*′-Vinyl-Bridged Porphyrin

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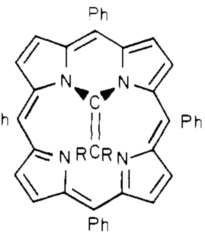
The complexation of metal ions by porphyrins (porphyrin metalation) has received considerable experimental study and invariably has led to the binding of metal ions to some or all of the pyrrole nitrogen atoms.[1] Recently we reported[2] that the *N*,*N*′-vinyl-bridged porphyrin **1**[3] underwent an unusual series of metalations with metal carbonyls. In these reactions one or both of the N–C (vinyl) bonds were ruptured (Scheme I). Now we report the structural characterization of a second product resulting from the reaction of **1** with triruthenium dodecacarbonyl. In this case again C–N bond rupture occurs, but now it involves one of the pyrrole C–N bonds.[4]



1, R = *p*-ClC$_6$H$_4$

Treatment of **1** with 2 mol of triruthenium dodecacarbonyl in boiling tetrahydrofuran for 3 h followed by evaporation and chromatography on silica gel with benzene as eluent yields a fraction from which orange **3** is readily crystallized since it is the least soluble component. However, preparative thin-layer chromatography of this fraction on silica gel with a 4:1 hexane/benzene eluent produces three bands, a rapidly eluting purple band followed by a red purple band and finally an orange band which contains **3**. The relative amounts of material in these three fractions vary from preparation to preparation. Orange **3** is the predominant product and has been obtained in yields up to ca. 50%. It has been possible to obtain up to a 30% yield of crystals of the new compound **5**[5] from the first band.

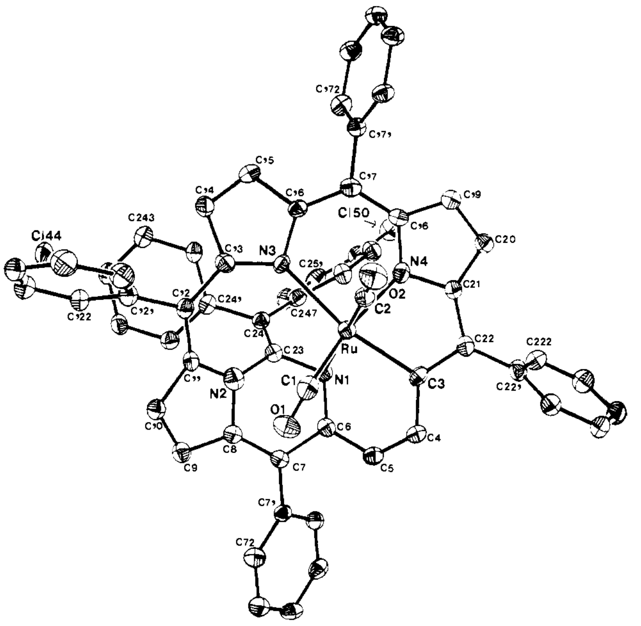


Figure 1. Perspective drawing of **5**. Some selected bond distances: Ru–C(1), 1.878 (7) Å; Ru–C(2), 1.864 (6) Å; Ru–C(3), 2.086 (6) Å; Ru–N(1), 2.206 (5) Å; Ru–N(3), 2.257 (6) Å; Ru–N(4), 2.068 (5) Å.

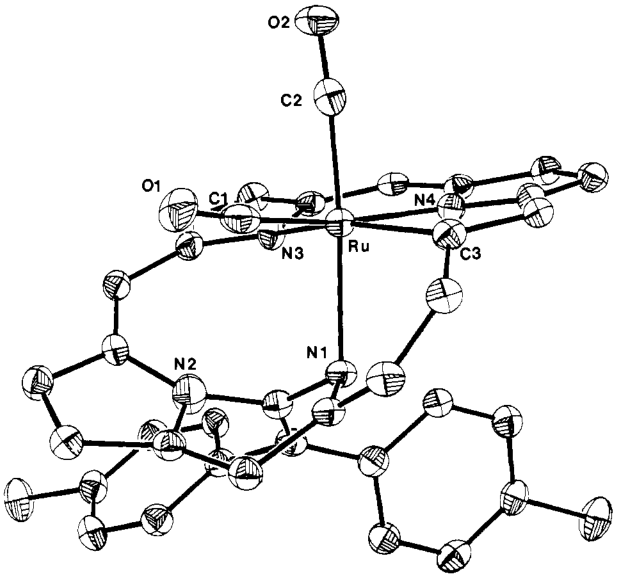
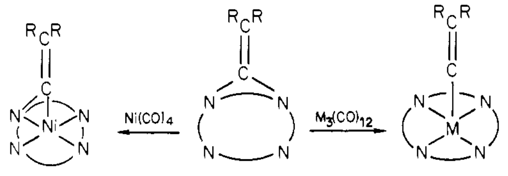


Figure 2. Drawing which shows how the damaged porphyrin is wrapped about the ruthenium atom. Four phenyl groups are omitted in this drawing.

Scheme I



4 1 2, M = Fe
3, M = Ru

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(1) Buchler, J. W. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, pp 390–483.

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(4) By way of contrast it should be remembered that the reaction between *meso*-tetraphenylporphyrin (TPPH$_2$) and triruthenium dodecacarbonyl yields, after recrystallization from chloroform/ethanol, (TPP)Ru(CO)(C$_2$H$_5$OH): Cullen, D.; Meyer, E., Jr.; Srivastava, T. S.; Tsutsui, M. *J. Chem. Soc., Chem. Commun.* **1972**, 584–585. Bonnett, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141–2149.

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