indicate that at room temperature the standard free energy differences for the three states of the system, namely $Eu^{II}$ + INA, $Eu^{II}$-INA complex, and $Eu^{III}$ + free radical, are small. This probably gives to the system its unusual stability for aqueous lanthanide species. The same remarks can be made for picolinic and nicotinic acids, except that in these cases reaction of the corresponding complexes with another europous ion does not take place. This implies that for these two acids not only the equilibrium constants $K_1$ but also the product of the rate constants $k_2k_3$ is considerably smaller. For explaining this, as well as the observation that the *N*-methyl derivative of isonicotinic acid gives a product of different nature than isonicotinic acid itself, it is not necessary to invoke new assumptions. It can be argued that the extent of charge transfer to the ligand is the factor that mainly determines not only the stability of the complexes but also the rate of their subsequent reduction and its path.

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# Crystal and Molecular Structure of the Free Base Porphyrin, Mesoporphyrin IX Dimethyl Ester

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**Abstract:** The structure of the free base porphyrin, mesoporphyrin IX dimethyl ester, has been determined from three-dimensional X-ray diffraction data. The porphyrin crystallizes with two molecules per unit cell in the triclinic space group $C_i^1$-$P\bar{1}$ with $a = 23.458\ (8)$ Å, $b = 11.378\ (4)$ Å, $c = 5.971\ (2)$ Å, $\alpha = 93.25\ (2)°$, $\beta = 94.23\ (2)°$, and $\gamma = 93.82\ (2)°$. The structure has been refined anisotropically to a final unweighted $R$ index (on $F^2$) of 0.072 based on 5107 measured intensities. The $R$ index (on $F$) for the 3336 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.049. Bond lengths and bond angles within the porphyrin core have been determined to estimated standard deviations of ±0.003 Å and ±0.2°, respectively. These bond lengths and angles closely resemble those in the porphyrin core of octaethylporphyrin. We conclude that the asymmetric pattern of substitution of mesoporphyrin IX dimethyl ester affects the bond lengths and bond angles within the porphyrin core to less than can be detected by this structure determination.

Complete X-ray crystallographic structure determinations of biologically important porphyrins,[1-3] corrins,[4-5] and pheophorbides[6-8] are relatively few in number. The asymmetric pattern of substitution of the naturally occurring compounds and the diverse nature of the substituents appear to make it difficult to obtain suitably crystalline samples. Nonetheless it is the asymmetry and substituent effects in these molecules which are of particular interest.

The structures of a number of symmetrically substituted free-base porphyrins have been reported[9-13] and some generalizations inferred about the structure of the porphyrin core.[11-13] Prior to this investigation no structure of a free-base biologically relevant porphyrin had been reported, although the structures of three metalloporphyrins had been determined.[1-3] The latter three structures were plagued with crystallographic problems which lowered the accuracy of the determinations. Two of the crystal structures contained a disordered porphyrin, while the third contained a disordered solvent molecule. In contrast to these structures the free-base form of mesoporphyrin IX dimethyl ester

Table II. Atomic Parameters for Mesoporphyrin IX Dimethyl Ester

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[a] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | −0.1663 (1) | 0.2579 (2) | −0.3144 (4) | 147 (5) | 808 (22) | 2995 (80) | 19 (8) | 83 (16) | 325 (33) |
| C(2) | −0.1279 (1) | 0.2477 (2) | −0.4911 (4) | 148 (5) | 955 (24) | 3043 (83) | 13 (9) | 107 (16) | 262 (35) |
| C(3) | −0.1044 (1) | 0.1411 (2) | −0.4766 (4) | 164 (5) | 919 (25) | 3049 (84) | 37 (9) | 138 (16) | 167 (36) |
| C(4) | −0.1283 (1) | 0.0834 (2) | −0.2936 (4) | 153 (5) | 817 (22) | 3108 (88) | 48 (8) | 126 (16) | 128 (34) |
| C(5) | −0.1175 (1) | −0.0268 (2) | −0.2227 (4) | 178 (5) | 842 (23) | 3406 (88) | 92 (9) | 161 (17) | 129 (36) |
| C(6) | −0.1421 (1) | −0.0859 (2) | −0.0520 (4) | 170 (5) | 745 (21) | 3192 (82) | 64 (8) | 95 (17) | 51 (33) |
| C(7) | −0.1283 (1) | −0.2021 (2) | 0.0159 (4) | 197 (5) | 723 (21) | 3584 (91) | 105 (9) | 94 (18) | 53 (35) |
| C(8) | −0.1618 (1) | −0.2272 (2) | 0.1867 (4) | 181 (5) | 718 (22) | 3724 (93) | 85 (8) | 112 (18) | 221 (35) |
| C(9) | −0.1954 (1) | −0.1253 (2) | 0.2211 (4) | 155 (5) | 701 (20) | 3164 (81) | 56 (8) | 83 (16) | 263 (33) |
| C(10) | −0.2335 (1) | −0.1150 (2) | 0.3871 (4) | 170 (5) | 680 (20) | 3243 (83) | 57 (8) | 116 (17) | 350 (33) |
| C(11) | −0.2656 (1) | −0.0202 (2) | 0.4385 (4) | 146 (4) | 707 (20) | 2953 (78) | 30 (8) | 53 (15) | 270 (32) |
| C(12) | −0.3038 (1) | −0.0103 (2) | 0.6146 (4) | 146 (4) | 728 (21) | 2712 (75) | 4 (8) | 68 (15) | 213 (31) |
| C(13) | −0.3267 (1) | 0.0967 (2) | 0.6042 (4) | 141 (4) | 697 (20) | 2621 (74) | 7 (7) | 75 (14) | 87 (30) |
| C(14) | −0.3028 (1) | 0.1550 (2) | 0.4215 (4) | 137 (4) | 674 (20) | 2633 (73) | 30 (7) | 70 (14) | 100 (30) |
| C(15) | −0.3142 (1) | 0.2650 (2) | 0.3490 (4) | 152 (5) | 663 (20) | 2721 (75) | 54 (8) | 57 (15) | 41 (31) |
| C(16) | −0.2904 (1) | 0.3217 (2) | 0.1743 (4) | 141 (4) | 616 (19) | 2687 (73) | 36 (7) | −5 (15) | 79 (30) |
| C(17) | −0.3057 (1) | 0.4367 (2) | 0.1016 (4) | 153 (5) | 615 (19) | 2685 (74) | 45 (7) | −13 (15) | 38 (30) |
| C(18) | −0.2726 (1) | 0.4623 (2) | −0.0681 (4) | 164 (5) | 627 (19) | 2995 (79) | 23 (8) | −28 (16) | 183 (31) |
| C(19) | −0.2377 (1) | 0.3624 (2) | −0.1004 (4) | 147 (4) | 666 (20) | 2621 (73) | 23 (7) | 29 (15) | 220 (30) |
| C(20) | −0.1992 (1) | 0.3523 (2) | −0.2663 (4) | 156 (4) | 767 (22) | 3236 (84) | 30 (8) | 86 (17) | 449 (34) |
| C(21) | −0.1157 (1) | 0.3389 (2) | −0.6558 (4) | 198 (6) | 1007 (26) | 3554 (93) | 35 (10) | 199 (19) | 504 (39) |
| C(22) | −0.0637 (1) | 0.4190 (3) | −0.5806 (6) | 254 (7) | 1158 (33) | 6994 (162) | −24 (12) | 67 (28) | 923 (59) |
| C(23) | −0.0615 (1) | 0.0920 (2) | −0.6234 (5) | 220 (6) | 1162 (29) | 4016 (102) | 91 (11) | 306 (20) | 277 (43) |
| C(24) | −0.0826 (1) | −0.2756 (2) | 0.0722 (5) | 275 (7) | 959 (27) | 4690 (113) | 204 (11) | 308 (23) | 275 (44) |
| C(25) | −0.0263 (1) | −0.2554 (4) | 0.0712 (6) | 260 (8) | 2171 (50) | 6091 (159) | 345 (16) | 299 (29) | 895 (71) |
| C(26) | −0.1654 (1) | −0.3363 (2) | 0.3147 (5) | 288 (7) | 856 (25) | 4944 (120) | 162 (11) | 252 (24) | 667 (44) |
| C(27) | −0.3151 (1) | −0.1025 (2) | 0.7778 (4) | 212 (6) | 922 (25) | 3712 (94) | 41 (10) | 219 (19) | 539 (38) |
| C(28) | −0.3700 (1) | 0.1457 (2) | 0.7500 (4) | 164 (5) | 754 (20) | 2650 (20) | 16 (8) | 128 (15) | 0 (31) |
| C(29) | −0.4309 (1) | 0.1173 (2) | 0.6461 (4) | 168 (5) | 1120 (26) | 2861 (80) | 33 (9) | 120 (16) | −243 (36) |
| C(30) | −0.4763 (1) | 0.1383 (2) | 0.8034 (4) | 177 (5) | 693 (21) | 2996 (86) | 36 (8) | 99 (17) | −48 (32) |
| C(31) | −0.3517 (1) | 0.5054 (2) | 0.1969 (4) | 205 (5) | 651 (20) | 2870 (77) | 85 (8) | 31 (16) | −3 (31) |
| C(32) | −0.4122 (1) | 0.4604 (2) | 0.0968 (4) | 174 (5) | 864 (23) | 3171 (86) | 93 (9) | 138 (17) | 61 (35) |
| C(33) | −0.4244 (1) | 0.4949 (2) | −0.1373 (4) | 161 (5) | 782 (23) | 3340 (88) | 94 (8) | 26 (16) | −170 (36) |
| C(34) | −0.2704 (1) | 0.5704 (2) | −0.1994 (5) | 233 (6) | 788 (23) | 3862 (97) | 62 (9) | 88 (20) | 512 (38) |
| C(35) | −0.5766 (1) | 0.1327 (2) | 0.8229 (3) | 170 (5) | 1258 (30) | 4542 (112) | 42 (10) | 246 (20) | −243 (46) |
| C(36) | −0.4495 (1) | 0.6549 (2) | −0.3535 (3) | 316 (8) | 1024 (28) | 3594 (101) | 122 (12) | −104 (22) | 224 (42) |
| O(1) | −0.4692 (1) | 0.1567 (2) | 1.0031 (3) | 211 (4) | 1643 (25) | 3141 (66) | 69 (8) | 146 (13) | −296 (31) |
| O(2) | −0.5280 (1) | 0.1300 (2) | 0.6896 (3) | 158 (3) | 1201 (19) | 3413 (61) | 43 (6) | 119 (12) | −144 (27) |
| O(3) | −0.4230 (1) | 0.4343 (2) | −0.3061 (3) | 431 (7) | 1113 (21) | 3557 (71) | 275 (9) | −87 (17) | −420 (31) |
| O(4) | −0.4366 (1) | 0.6079 (2) | −0.1394 (3) | 344 (5) | 852 (17) | 3290 (62) | 179 (7) | −137 (14) | −56 (25) |
| N(1) | −0.1655 (1) | 0.1568 (2) | −0.2022 (3) | 164 (4) | 801 (18) | 3005 (67) | 52 (7) | 172 (13) | 275 (28) |
| N(2) | −0.1827 (1) | −0.0411 (2) | 0.0752 (3) | 162 (4) | 732 (17) | 3077 (68) | 73 (7) | 133 (13) | 193 (28) |
| N(3) | −0.2664 (1) | 0.0813 (2) | 0.3274 (3) | 155 (4) | 665 (16) | 2912 (62) | 54 (6) | 170 (12) | 283 (26) |
| N(4) | −0.2494 (1) | 0.2785 (2) | 0.0485 (3) | 140 (4) | 663 (16) | 2879 (63) | 43 (6) | 79 (12) | 220 (26) |

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The anisotropic thermal parameters have been multiplied by $10^5$. Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures.

(MP-IX DME)[14] crystallizes in a fully ordered structure which allows, for the first time, an assessment of possible asymmetry in the porphyrin core.

## Experimental Section

Crystals of mesoporphyrin IX dimethyl ester were prepared by diffusing methanol into chloroform solutions of the porphyrin ester (obtained from Sigma Chemical Co.) over an 8 month period. The crystals grew as a large clump of well-formed needles at the interface of the two solvents. Preliminary Weissenberg photographs taken with Cu K$\alpha$ radiation showed only the required center of symmetry and hence the space group is either $P1$ or $P\bar{1}$. The crystal selected for data collection was a large needle which was cut perpendicular to its major axis to give a pseudo-parallelepiped with major, bounding faces of the forms {100}, {010}, and {001}. The distances between the faces of these forms are 0.025, 0.183, and 1.07 mm. The crystal was mounted with the $c^*$ axis approximately along the spindle axis.

The lattice parameters, obtained as previously described[15] by hand-centering of 14 reflections on a FACS-I diffractometer using Cu K$\alpha_1$ radiation ($\lambda$ 1.540562 Å) in the range $38 \leq 2\theta \leq 57°$, are $a$ = 23.458 (8) Å, $b$ = 11.378 (4) Å, $c$ = 5.971 (2) Å, $\alpha$ = 93.25 (2)°, $\beta$ = 94.23 (2)°, and $\gamma$ = 93.82 (2)°. The calculated density, based on two molecules of porphyrin per unit cell, is 1.235 g/cm$^3$ and agrees well with an observed value of 1.24 (1) g/cm$^3$, as measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of $2\theta$ by the $\theta$-$2\theta$ scan method using Cu K$\alpha$ radiation prefiltered with Ni foil. The scan range in $2\theta$ was from 1.0° below the Cu K$\alpha_1$ peak to 1.0° above the Cu K$\alpha_2$ peak. The takeoff angle was 2.8° and the receiving counter was positioned 33 cm from the crystal with an aperture 5.0 mm high and 5.0 mm wide. Initially background counts of 20 sec were taken at the each end of the scan range. Past a $2\theta$ of 50° this was increased to 40 sec. A scan rate of 2° in $2\theta$ per minute was used. Data were collected in the range $2 < 2\theta \leq 126°$. Data collection was terminated when less than 10% of the measured reflections were statistically observable. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. The deviations of these standards were all within counting statistics.

The data were processed as previously described using a value of 0.05 for $p$.[15] Of the 6290 reflections measured, 5107 are unique and of these 3336 have $F_o^2 > 3\sigma(F_o^2)$ and were used in initial refinements. Data were collected with $l \geq -1$, and as a result 1176 Friedel pairs were measured. The 1176 pairs of reflections deviate by 1.8% from their average values. Sample calculations[16] for an absorption correction were made using a linear absorption coefficient of 6.19 cm$^{-1}$. The transmission factors calculated ranged from 0.87 to 0.98, and an absorption correction was therefore applied.

**Solution and Refinement of the Structure.** Normalized structure factors ($|E|$'s) scaled such that $\langle E^2 \rangle = 1.0$ were calculated from the measured structure amplitudes. The statistical distribution of

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

| Atom | Min | Inter | Max |
|---|---|---|---|
| C(1) | 0.199 (3) | 0.214 (3) | 0.246 (3) |
| C(2) | 0.198 (3) | 0.230 (3) | 0.254 (3) |
| C(3) | 0.205 (3) | 0.236 (3) | 0.246 (3) |
| C(4) | 0.199 (3) | 0.230 (3) | 0.240 (3) |
| C(5) | 0.201 (3) | 0.239 (3) | 0.255 (3) |
| C(6) | 0.203 (3) | 0.229 (3) | 0.240 (3) |
| C(7) | 0.196 (3) | 0.247 (3) | 0.254 (3) |
| C(8) | 0.199 (3) | 0.232 (3) | 0.261 (3) |
| C(9) | 0.198 (3) | 0.213 (3) | 0.243 (3) |
| C(10) | 0.197 (3) | 0.213 (3) | 0.251 (3) |
| C(11) | 0.200 (3) | 0.205 (3) | 0.237 (3) |
| C(12) | 0.196 (3) | 0.212 (3) | 0.229 (3) |
| C(13) | 0.195 (3) | 0.214 (3) | 0.218 (3) |
| C(14) | 0.193 (3) | 0.209 (3) | 0.218 (3) |
| C(15) | 0.194 (3) | 0.215 (3) | 0.222 (3) |
| C(16) | 0.191 (3) | 0.203 (3) | 0.223 (3) |
| C(17) | 0.193 (3) | 0.204 (3) | 0.227 (3) |
| C(18) | 0.198 (3) | 0.208 (3) | 0.240 (3) |
| C(19) | 0.198 (3) | 0.203 (3) | 0.224 (3) |
| C(20) | 0.201 (3) | 0.207 (3) | 0.257 (3) |
| C(21) | 0.211 (3) | 0.241 (3) | 0.279 (3) |
| C(22) | 0.242 (4) | 0.273 (4) | 0.368 (4) |
| C(23) | 0.217 (4) | 0.266 (4) | 0.294 (4) |
| C(24) | 0.207 (4) | 0.269 (4) | 0.318 (4) |
| C(25) | 0.226 (4) | 0.311 (4) | 0.405 (4) |
| C(26) | 0.206 (4) | 0.267 (4) | 0.323 (4) |
| C(27) | 0.210 (3) | 0.240 (3) | 0.282 (3) |
| C(28) | 0.200 (3) | 0.217 (3) | 0.232 (3) |
| C(29) | 0.203 (3) | 0.225 (3) | 0.282 (3) |
| C(30) | 0.205 (3) | 0.222 (3) | 0.238 (3) |
| C(31) | 0.195 (3) | 0.226 (3) | 0.247 (3) |
| C(32) | 0.199 (3) | 0.241 (3) | 0.248 (3) |
| C(33) | 0.190 (3) | 0.224 (3) | 0.262 (3) |
| C(34) | 0.206 (4) | 0.253 (3) | 0.276 (3) |
| C(35) | 0.202 (4) | 0.268 (4) | 0.312 (4) |
| C(36) | 0.229 (4) | 0.263 (4) | 0.311 (4) |
| O(1) | 0.218 (2) | 0.250 (2) | 0.335 (2) |
| O(2) | 0.204 (2) | 0.242 (2) | 0.288 (2) |
| O(3) | 0.216 (3) | 0.262 (3) | 0.374 (3) |
| O(4) | 0.216 (2) | 0.233 (2) | 0.330 (2) |
| N(1) | 0.199 (3) | 0.218 (3) | 0.249 (3) |
| N(2) | 0.196 (3) | 0.218 (3) | 0.243 (3) |
| N(3) | 0.193 (3) | 0.198 (3) | 0.243 (3) |
| N(4) | 0.193 (3) | 0.204 (3) | 0.231 (3) |

$|E|$'s found closely resembles that for a centric crystal, suggesting that the correct space group is $P\bar{1}$.

Using the quantities $|E^2 - 1|$ a sharpened, origin removed Patterson map was calculated and the orientation of the porphyrin plane was obtained. The position of the two molecules in the cell was calculated from the $2x$, $2y$, $2z$ vector, 10.8 Å in length, which corresponded to the sum of all the interplanar, porphyrin–porphyrin vectors. A difference Fourier map phased on the 24 atoms of the porphyrin core revealed the positions of a further 15 atoms. The positions of the remaining five atoms were obtained from a second difference Fourier map. Three cycles of least-squares refinement of the positional parameters for the 44 non-hydrogen atoms reduced $R$ and $R_w$ to 0.22 and 0.28.[17] The structure was refined by full-matrix, least-squares techniques. Values of the atomic scattering factors and the anomalous terms[18] were taken from the usual sources

The H atoms at the methine (C–H = 0.95 Å), methylene (C–H = 1.0 Å), and the amine pyrrole (N–H = 0.95 Å) positions were idealized, and thermal parameters were assigned so that $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å$^2$. The contributions of these hydrogen atoms were then added as fixed contributions to the next cycle of refinement. Owing to the very large number of variables (397) no attempt was made to refine the positions of the amine pyrrole hydrogen atoms, as was possible in the centrosymmetric OEP free-base molecule.[13] Three cycles of anisotropic, full-matrix, least-squares refinement of the 44 non-hydrogen atoms converged with $R$ and $R_w$ equal to 0.049 and 0.066, respectively, for 3336 observations and 397 variables. In an attempt to decrease the estimated standard deviations one further cycle of anisotropic full-matrix least-squares on $F^2$ rather than $F$, was carried out. This refinement used all 5107 measured intensities (including those with $F_o^2 < 0$), and converged to values of $R$ and $R_w$ (on $F^2$) of 0.072 and 0.14, respectively. In this calculation the resultant estimated standard deviations were reduced from those in the previous cycle by about 30%, as would be predicted from the increase in the number of observations.

An analysis of $|F_o|$ and $|F_c|$ as a function of setting angles, magnitude of $|F_o|$, and Miller indices showed no unusual trends. The standard deviation of an observation of unit weight is 1.50 e. A final difference Fourier map revealed no significant features. The values of $F_o^2$ and $F_c^2$ are given in Table I.[19]

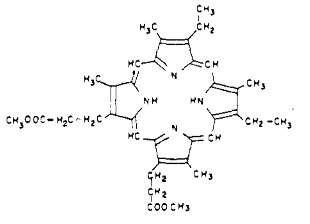
The final atomic parameters and their errors are listed in Table II. The calculated atomic parameters for the hydrogen atoms are given in Table III.[19] Table IV presents the root-mean-square amplitudes of thermal vibration.

## Description and Discussion of the Structure

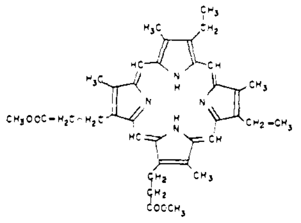
The crystal structure consists of discrete molecules of MP-IX DME. The carbomethoxy groups of adjacent molecules are arranged pairwise, with their symmetry equivalents, about centers of symmetry at ½,½,½ and ½,0,½ as is illustrated in Figure 1. As a result there are the following short nonbonded contacts: O(1)–H2C(32) (2.71 Å), O(3)–H2C(31) (2.65 Å), and O(3)–H1C(28) (2.85 Å). The shortest H···H intermolecular contact is H2C(31)···H2C(34) of 2.42 Å. The shortest contact made by a pyrrole nitrogen atom is between N(2) and H3C(27) (2.88 Å). All of the methyl and methylene hydrogen atoms are staggered, as expected.

The numbering scheme[20] used in this paper is illustrated and a general view of the molecule is shown in Figure 2. The individual and averaged bond distances and angles are presented in Table V.

The structure of the porphyrin core of MP-IX DME is essentially the same as that found in other free-base porphyrins.[9-13] The porphyrin contains isolated imino and amino pyrrole moieties and as a result the pyrrole rings in the molecule are nonequivalent. As observed in other free-base porphyrins, the hydrogen atoms of the core are localized on opposing amino pyrrole rings. Because of this and because of the asymmetric pattern of substitution in MP-IX there are two possible geometric isomers (**1** and **2**). In essence, these isomers differ only in the placement of the amino hydrogen atoms in the center of the macrocycle. The structure reported here is that of the resonance hybrid of isomer **2**.[21] There does not appear to be any apparent chemical rationale why **2** is favored over **1**. In the crystal it is likely that the stereochemical differences between the imino and amino pyrrole rings are so great as to preclude the presence of both isomers. In solution rapid N–H tautomerism is observed.[22]



1



2

The 24-atom porphyrin core is nearly planar; the largest out-of-plane displacement being 0.07 Å for C(17) (Table VI). The individual pyrrole rings are canted with respect to each other by from 1 to 3°. The two trans amino pyrrole rings are *alternately* tilted above and below the plane of the macrocycle, thus minimizing transannular interactions.

The transannular separation of the N–H hydrogen atoms is calculated to be 2.05 Å. This is significantly shorter than

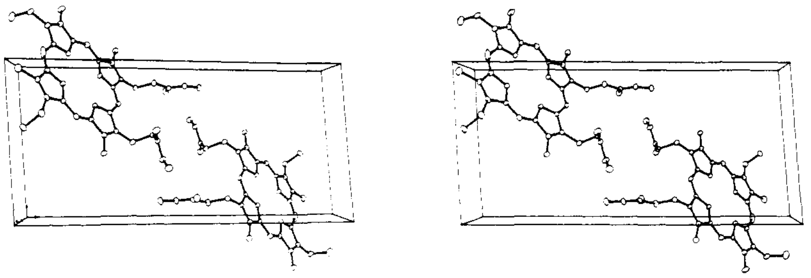


Figure 1. Stereoscopic view of the packing of the molecules in the crystal. For clarity the hydrogen atoms have been omitted from the drawing.

Table V. Bond Distances (A) and Angles (deg) in MP-IX DME[a]

| | | | Average[b] | | | | Average[b] |
|---|---|---|---|---|---|---|---|
| N(1)–C(1) | 1.364 | N–$C_a$[c] | 1.366 (3) | C(30)–O(2) | 1.342 | | |
| N(1)–C(4) | 1.369 | | | C(33)–O(4) | 1.336 | | |
| N(2)–C(6) | 1.367 | | | O(2)–C(35) | 1.439 | | |
| N(2)–C(9) | 1.364 | | | O(3)–C(36) | 1.433 | | |
| N(3)–C(11) | 1.365 | | | C(1)–N(1)–C(4) | 109.8 | $C_a$–N–$C_a$ | 109.8 (2) |
| N(3)–C(14) | 1.365 | | | C(11)–N(3)–C(14) | 109.9 | | |
| N(4)–C(16) | 1.362 | | | C(6)–N(2)–C(9) | 105.6 | | 105.7 (2) |
| N(4)–C(19) | 1.369 | | | C(16)–N(4)–C(19) | 105.8 | | |
| C(5)–C(4) | 1.379 | $C_m$–$C_a$ | 1.388 (3) | N(1)–C(1)–C(2) | 107.6 | N–$C_a$–$C_b$ | 107.5 (2) |
| C(5)–C(6) | 1.391 | | | N(1)–C(4)–C(3) | 107.5 | | |
| C(10)–C(9) | 1.388 | | | N(3)–C(11)–C(12) | 107.4 | | |
| C(10)–C(11) | 1.389 | | | N(3)–C(14)–C(13) | 107.5 | | |
| C(15)–C(14) | 1.383 | | | N(2)–C(6)–C(7) | 111.0 | | 110.9 (2) |
| C(15)–C(16) | 1.390 | | | N(2)–C(9)–C(8) | 111.1 | | |
| C(20)–C(19) | 1.395 | | | N(4)–C(16)–C(17) | 110.7 | | |
| C(20)–C(1) | 1.392 | | | N(4)–C(19)–C(18) | 110.8 | | |
| C(1)–C(2) | 1.442 | $C_a$–$C_b$ | 1.438 (3) | C(1)–C(2)–C(21) | 125.6 | $C_a$–$C_b$–$C_{alkyl}$ | 125.3 (3) |
| C(3)–C(4) | 1.435 | | | C(4)–C(3)–C(23) | 125.5 | | |
| C(11)–C(12) | 1.436 | | | C(6)–C(7)–C(24) | 126.7 | | |
| C(13)–C(14) | 1.438 | | | C(9)–C(8)–C(26) | 125.5 | | |
| C(6)–C(7) | 1.455 | $C_a$–$C_b$ | 1.457 (3) | C(11)–C(12)–C(27) | 124.8 | | |
| C(8)–C(9) | 1.457 | | | C(14)–C(13)–C(28) | 125.1 | | |
| C(16)–C(17) | 1.461 | | | C(16)–C(17)–C(31) | 124.2 | | |
| C(18)–C(19) | 1.456 | | | C(19)–C(18)–C(34) | 125.2 | | |
| C(2)–C(3) | 1.369 | $C_b$–$C_b$ | 1.364 (4) | C(3)–C(2)–C(21) | 127.1 | $C_b$–$C_b$–$C_{alkyl}$ | 127.7 (3) |
| C(7)–C(8) | 1.365 | | | C(2)–C(3)–C(23) | 126.8 | | |
| C(12)–C(13) | 1.366 | | | C(8)–C(7)–C(24) | 126.9 | | |
| C(17)–C(18) | 1.354 | | | C(7)–C(8)–C(26) | 128.4 | | |
| C(3)–C(23) | 1.498 | $C_b$–$C_{methyl}$ | 1.496 (3) | C(13)–C(12)–C(27) | 127.5 | | |
| C(8)–C(26) | 1.494 (4) | | | C(12)–C(13)–C(28) | 127.3 | | |
| C(12)–C(27) | 1.495 | | | C(18)–C(17)–C(31) | 129.2 | | |
| C(18)–C(34) | 1.495 | | | C(17)–C(18)–C(34) | 128.5 | | |
| C(2)–C(21) | 1.498 | Ethyl | 1.505 (5) | C(2)–C(21)–C(22) | 112.4 | | |
| C(7)–C(24) | 1.508 | | | C(7)–C(24)–C(25) | 112.0 | | |
| C(21)–C(22) | 1.498 (4) | | | C(13)–C(28)–C(29) | 111.6 | | |
| C(24)–C(25) | 1.517 (5) | | | C(28)–C(29)–C(30) | 114.4 | | |
| C(13)–C(28) | 1.500 | Propionate | | C(29)–C(30)–O(1) | 126.4 | | |
| C(17)–C(31) | 1.500 | | | C(29)–C(30)–O(2) | 110.2 | | |
| C(28)–C(29) | 1.521 | | | C(30)–O(2)–C(35) | 116.3 | | |
| C(31)–C(32) | 1.543 | | | C(17)–C(31)–C(32) | 112.5 | | |
| C(29)–C(30) | 1.493 | | | C(31)–C(32)–C(33) | 112.6 | | |
| C(32)–C(33) | 1.486 (4) | | | C(32)–C(33)–O(3) | 127.0 | | |
| C(30)–O(1) | 1.196 | | | C(32)–C(33)–O(4) | 110.9 | | |
| C(33)–O(3) | 1.192 | | | C(33)–O(4)–C(36) | 117.8 | | |

[a] The errors in all the bond distances, and in all the bond angles, unless otherwise indicated, are respectively ±0.003 A and ±0.2°. [b] The figure in parentheses following an average value is the larger of the standard deviations estimated for an individual value from the inverse matrix or on the assumption that the values averaged are from the same population. [c] The notation $C_a$, $C_b$, and $C_m$ is that of J. L. Hoard, *Science*, **174**, 1295 (1971).

that found in OEP (2.36 (4) Å)[13] and in porphine (2.41 Å).[11] In Table VII we list a number of transannular distances which serve to describe the geometry of the porphyrin core in MP-IX DME, OEP, and porphine. As may be seen the N-N as well as the N-H separations in MP-IX DME are short compared with those in the other two free-base porphyrins. The large differences in the transanular separations exist despite apparently identical bond distances and bond angles in the three porphyrins. Rather than reflecting any real differences in the size of the macrocycles, these parameters show that there are significant differences in the conformations of the three molecules. An examination of the deviations from planarity in these porphyrins shows that both OEP and porphine have an essentially centrosymmetric conformation, in which opposing pyrrole nitrogen atoms are alternately above and below the plane of the macrocycle. In MP-IX DME the conformation is more complex. In relation to an imaginary C(5)-C(15) axis, the nitrogen atoms of the four pyrrole rings are all tilted upward (Table VI).

Table VI. Deviations in Units of 0.001 A and Equations of Weighted Least-Squares Planes[a]

| | Plane 1 | Plane 2 | Plane 3 | Plane 4 | Plane 5 | Plane 6 | Plane 7 |
|---|---|---|---|---|---|---|---|
| C(1) | 16 (2) | 6 (2) | | | | | |
| C(2) | −26 (2) | −5 (2) | | | | 0 (0) | |
| C(3) | −12 (2) | 2 (2) | | | | | |
| C(4) | 25 (2) | 3 (2) | | | | | |
| C(5) | 21 (2) | −20 | −5 | | | | |
| C(6) | −1 (2) | | −2 (2) | | | | |
| C(7) | 11 (2) | | 3 (2) | | | | 0 (0) |
| C(8) | −24 (3) | | −2 (2) | | | | |
| C(9) | −46 (2) | | 0 (2) | | | | |
| C(10) | −36 (2) | | 45 | −9 | | | |
| C(11) | −5 (2) | | | −1 (2) | | | |
| C(12) | 38 (2) | | | 1 (2) | | | |
| C(13) | 47 (2) | | | −1 (2) | | | |
| C(14) | 14 (2) | | | 0 (2) | | | |
| C(15) | 1 (2) | | | −10 | 23 | | |
| C(16) | −10 (2) | | | | 4 (2) | | |
| C(17) | −66 (2) | | | | −4 (2) | | |
| C(18) | −33 (2) | | | | 3 (2) | | |
| C(19) | 25 (2) | | | | 0 (2) | | |
| C(20) | 22 (2) | 9 | | | −45 | | |
| C(21) | −56 | 0 | | | | 0 (0) | |
| C(22) | 1310 | | | | | 0 (0) | |
| C(23) | −28 | 10 | | | | | |
| C(24) | 146 | | 104 | | | | 0 (0) |
| C(25) | 1589 | | | | | | 0 (0) |
| C(26) | −51 | | −21 | | | | |
| C(27) | 72 | | | 11 | | | |
| C(28) | 54 | | | −33 | | | |
| C(31) | −200 | | | | −76 | | |
| C(34) | −42 | | | | 23 | | |
| N(1) | 31 (2) | −4 (2) | | | | | |
| N(2) | −31 (2) | | 1 (2) | | | | |
| N(3) | −16 (2) | | | 0 (2) | | | |
| N(4) | 36 (2) | | | | −2 (2) | | |

| Plane | A | B | C | D |
|---|---|---|---|---|
| 1 | 1.559 | 3.750 | 3.413 | −2.714 porphyrin |
| 2 | 1.586 | 3.870 | 3.290 | −2.680 pyrrole 1 |
| 3 | 1.515 | 3.813 | 3.515 | −2.661 pyrrole 2 |
| 4 | 1.604 | 3.734 | 3.284 | −2.894 pyrrole 3 |
| 5 | 1.490 | 4.112 | 3.485 | −2.402 pyrrole 4 |
| 6 | −1.531 | 7.230 | 2.870 | 2.339 ethyl |
| 7 | −6.536 | −8.587 | 3.779 | 2.634 ethyl |

Angles between the Normals to the Planes

| Plane A | Plane B | Angle (deg) |
|---|---|---|
| 1 | 2 | 1.4 |
| 1 | 3 | 1.4 |
| 1 | 4 | 1.6 |
| 1 | 5 | 2.5 |
| 1 | 6 | 84.6 |
| 1 | 7 | 96.2 |
| 2 | 3 | 2.7 |
| 2 | 4 | 0.8 |
| 2 | 5 | 3.1 |
| 3 | 4 | 3.0 |
| 3 | 5 | 1.6 |
| 2 | 6 | 85.2 |
| 3 | 7 | 95.6 |

[a] The entries for which an error is *not* indicated are for atoms which were not included in the calculation of the plane. [b] The plane is in triclinic coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

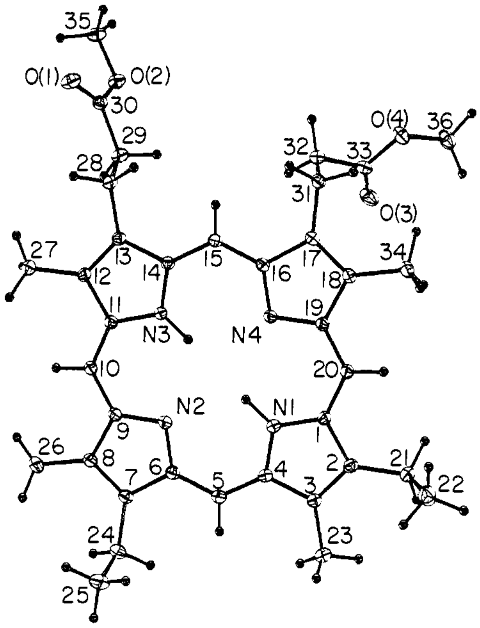


Figure 2. Drawing to indicate the numbering sequence used in this paper for the 44 independent non-hydrogen atoms. The thermal ellipsoids are drawn at the 50% probability level, with exception of those for the hydrogen atoms which have been reduced for clarity.

Table VII. Transannular Distances (A) in Three Free-Base Porphyrins

| Atoms | OEP[a] | Porphine[b] | MP-IX DME[c] |
|---|---|---|---|
| HN(1)–HN(3) | 2.36 (4) | 2.41 (4) | 2.05 (10) |
| N(1)–N(3) | 4.052 | 4.058 | 3.941 |
| N(2)–N(4) | 4.195 | 4.112 | 4.077 |
| N(1)–N(2) | 2.916 | 2.889 | 2.862 |
| N(2)–N(3) | 2.917 | 2.901 | 2.811 |
| N(3)–N(4) | 2.916 | 2.879 | 2.861 |
| N(4)–N(1) | 2.917 | 2.886 | 2.806 |
| C(5)–C(15) | 6.844 | 6.834 | 6.574 |
| C(10–C(20) | 6.841 | 6.853 | 6.747 |
| C(5)–C(10) | 4.849 | 4.862 | 4.538 |
| C(10)–C(15) | 4.828 | 4.822 | 4.868 |
| C(15)–C(20) | 4.849 | 4.860 | 4.550 |
| C(20)–C(5) | 4.828 | 4.814 | 4.872 |

[a] Reference 13, the errors on the C–C and N–N distances are ±0.002 A. [b] Reference 11, estimated errors of ±0.007 A. [c] This work, estimated errors of ±0.004 A.

Cullen and Meyer[23] have made an interesting comparison of two conformations of the OEP molecule, as observed in two crystalline modifications of Ni(OEP).[23,24] In the two forms there are 30° differences in the twists of the pyrrole rings, which are accompanied by 0.03 Å differences in the Ni-N bond lengths. The shorter Ni-N bond lengths are found in the more highly puckered form of Ni(OEP). Despite the fact that these structural alterations are accompanied by some significant changes in the bond lengths of the porphyrin core the conclusion must be drawn that the size of the porphyrin "bite" is variable, owing to the conformational flexibility of the porphyrin ring.[25] The short transannular distance in MP-IX DME is another demonstration of this phenomenon.

The bond lengths and bond angles (Table V) in the porphyrin core of MP-IX DME are normal[13] and do not appear to reflect the asymmetric pattern of substitution about the periphery of the molecule. Furthermore, the averaged parameters obtained from this determination are identical with those found in OEP[13] and porphine.[11] (Table VIII). Differences in the $C_a$-$C_b$ bond lengths between the amino and imino pyrrole rings are observed in the three structures. It is tempting to discern a small variation in the $C_b$-$C_b$ bond lengths in MP-IX DME, but the differences are at the limit of accuracy of this determination, particularly in view of the large variation in the two presumably equivalent imino pyrrole $C_b$-$C_b$ bond lengths. It is perhaps noteworthy that pyrrole 4, which is twisted by 2.4° from the plane of the macrocycle (compared with an average tilt of 1.5° for the other three pyrrole rings), has associated with it an ano-

Table VIII. Average Bond Distances and Bond Lengths for Several Porphyrins[a]

| Bond[b] | TPrP[c] | Porphine[d] | OEP[e] | MP-IX DME[f] |
|---|---|---|---|---|
| | | Imino Pyrrole Ring | | |
| $N-C_a$ | 1.372 | 1.374 | 1.364 (2) | 1.366 (3) |
| $C_a-C_b$ | 1.443 | 1.452 | 1.462 (2) | 1.457 (3) |
| $C_b-C_b$ | 1.341 | 1.345 | 1.353 (2) | 1.359 (5) |
| $C_a-N-C_a$ | 106.6 | 106.1 | 105.7 (2) | 105.7 (2) |
| $N-C_a-C_b$ | 109.5 | 109.8 | 110.8 (2) | 110.9 (2) |
| $C_a-C_b-C_b$ | 107.3 | 107.1 | 106.3 (2) | 106.3 (2) |
| $N-C_a-C_m$ | 126.4 | 125.0 | 125.1 (2) | 124.7 (3) |
| $C_b-C_a-C_m$ | 124.5 | 125.1 | 124.0 (2) | 124.4 (3) |
| | | Amino Pyrrole Ring | | |
| $N-C_a$ | 1.376 | 1.380 | 1.367 (2) | 1.365 (3) |
| $C_a-C_b$ | 1.437 | 1.431 | 1.438 (2) | 1.438 (3) |
| $C_b-C_b$ | 1.352 | 1.365 | 1.373 (2) | 1.368 (3) |
| $C_a-C_m$ | 1.397 | 1.382 | 1.392 (2) | 1.388 (3) |
| $C_a-N-C_a$ | 110.0 | 108.6 | 109.6 (2) | 109.8 (2) |
| $N-C_a-C_b$ | 106.7 | 107.9 | 107.7 (2) | 107.5 (2) |
| $C_a-C_b-C_b$ | 108.3 | 107.9 | 107.4 (2) | 107.6 (2) |
| $N-C_a-C_m$ | 127.1 | 125.5 | 125.0 (2) | 125.3 (2) |
| $C_b-C_a-C_m$ | 126.2 | 126.9 | 127.3 (2) | 127.2 (2) |
| $C_a-C_m-C_a$ | 125.0 | 127.1 | 127.6 (2) | 127.7 (2) |

[a] Bond lengths are in angstroms and bond angles in degrees. [b] Defined in text. [c] Reference 12. Errors: 0.004 A and 0.2–0.4°. [d] Reference 11. Errors: 0.004–0.007 A and 0.3–0.5°. [e] Reference 13. [f] This work.

malously short $C_b$-$C_b$ distance of 1.354 (2) Å. The average of the other three $C_b$-$C_b$ distances is 1.367 (2) Å. The intermolecular contacts made by the methyl propionate chain on this ring appear to be the cause of the increased twisting of this pyrrole. Table VIII also gives the averaged parameters for the meso tetrasubstituted porphyrin, tetrapropyloporphine.[11] The structure of MP-IX DME again demonstrates[13] that there are significant, but small differences between the meso tetrasubstituted porphyrins and the octaalkyl porphyrins. These differences involve both the bond lengths and bond angles. For example the $C_a$-$C_m$-$C_a$ angle is 2-3° smaller in the meso substituted porphyrins than in the octaalkyl porphyrins. These differences persist in the metalloporphyrins, as is demonstrated by the structures of $SnCl_2(TPP)$[26] and $SnCl_2(OEP)$.[27] The smaller $C_a$-$C_m$-$C_a$ angle in the meso substituted porphyrins does not result in a significantly smaller central hole for these porphyrins as compared with that in the octaalkyl porphyrins, because of compensating changes in the other bond angles and bond lengths in the macrocycle. For example, the Sn-N bond lengths in $SnCl_2(OEP)$ are 0.01 Å shorter than those in the TPP complex. The structure of the free base, MP-IX DME, compares favorably with the structures of Ni(MP-IX DME) and Fe(DP-IX DME)($OCH_3$) reported by Hoard.[2,3] Within the limits imposed by the accuracy of the metalloporphyrin structures the asymmetric pattern of substitution of the porphyrin ring appears to have no effect on the structure of the molecule, although it may well manifest itself in the electronic structure.[28]

A comparison of the structure of MP-IX DME with that of PP-IX, as observed in three ferric complexes (Fe(Cl)(PP-IX),[1] $Fe(1\text{-Me-Im})_2(PP\text{-IX})$,[29] and $Fe(SC_6H_4NO_2)(PP\text{-IX-DME})$[30]) indicates that the substitution of ethyl groups at C(2) and C(7) for the vinyl groups found in PP-IX has relatively little stereochemical consequence. Both groups are forced to lie out of the plane of the porphyrin macrocycle because of short intramolecular contacts between adjacent methyl, methylene, or vinyl groups. In MP-IX DME the average dihedral angle between the three-atom plane of the ethyl group and the plane of the porphyrin is 84.8°. The equivalent dihedral angle in the PP-IX structures varies between 28 and 50°. Because of the smaller twist of the vinyl groups and because of the tetrahedral hybridization of the carbon atoms in the ethyl groups the MP-IX molecule has a slightly greater above-plane width than PP-IX at the C(2) and C(7) positions. Despite the fact that the vinyl groups are not coplanar with the porphyrin, their presence does affect the electronic structure of the porphyrin molecule. The absorption maxima[31] in MP-IX DME are shifted by 5-10 nm toward shorter wavelengths from those for PP-IX DME.

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**Supplementary Material Available.** Tables I and III will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5363.

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(17) In the refinement of $F$ the quantity minimized is $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights $w$ are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The error in an observation of unit weight is defined as $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ where $n$ is the number of observations and $m$ is the number of variables. In the refinement on $F^2$ the quantity minimized is $\Sigma w(F_o^2 - F_c^2)^2$, where $F_o^2$ and $F_c^2$ are the observed and calculated structure amplitudes and where the weights, $w$, are taken as $1/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \Sigma|F_o^2 - F_c^2|/\Sigma|F_o^2|$ and $R_w = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$. The error in an observation of unit weight is defined as $[\Sigma w(F_o^2 - F_c^2)^2(n - m)]^{1/2}$.

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# Phenyldiazene Complexes. Structure and Spectra of Chlorodicarbonyl(*cis*-phenyldiazene)bis(triphenylphosphine)ruthenium(II) Perchlorate Methylene Chloride Solvate

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**Abstract:** The structure of $[RuCl(CO)_2(HN_2C_6H_5)(P(C_6H_5)_3)_2][ClO_4]\cdot CH_2Cl_2$ has been determined by X-ray diffraction methods. The compound crystallizes from methylene chloride as solvated crystals in space group $C_{2h}^5 - P2_1/c$ with four formula units in a cell of dimensions $a = 11.801$ (5) Å, $b = 17.752$ (8) Å, $c = 22.938$ (11) Å, and $\beta = 110.96$ (2)°. Based on 5074 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure has been solved and refined by full-matrix, least-squares methods to an $R$ index (on $F$) of 0.053. The structure consists of discrete ions and solvent molecules. The ruthenium cation is six-coordinate, with trans phosphine ligands and cis carbonyl ligands. The phenyldiazene ligand adopts the cis configuration about the N-N double bond and is bound in a $\sigma$ fashion through N(1) to the metal. The positional parameters of the nonaromatic diazene proton were refined. Important angles and distances are Ru-N(1) = 2.086 (5) Å, N(1)-N(2) = 1.218 (7) Å, N(1)-H = 1.00 (6) Å, N(2)-C(phenyl) = 1.409 (6) Å, ∠Ru-N(1)-N(2) = 129.2 (5)°, ∠Ru-N(1)-H = 128 (4)°, ∠H(1)-N(1)-N(2) = 102 (4)°, and ∠N(1)-N(2)-C(phenyl) = 118.2 (5)°. The short, nonbonded contact between the nonaromatic diazene proton and an ortho-phenyl proton causes considerable rotation of the phenyl group about the N-C bond. Spectroscopic and structural data suggest that phenyldiazene behaves as a normal $\sigma$-donor ligand without significant $\pi$-bonding characteristics. The N-N stretching frequencies for $PtCl(HN_2C_6H_5)(P(C_2H_5)_3)_2^+$, the title complex, and their respective deprotonated analogs are shown to be coupled with vibrational modes of the phenyl groups. The values of $\nu$(NN) for the diazenido complexes are shown to be lower than those for the corresponding diazene complexes.

Aryldiazo and aryldiazene ligands have been of great interest in recent years because of their close relationship to dinitrogen and nitrosyl ligands. Recent work has shown that diazo ligands can be prepared from coordinated dinitrogen in Re, Mo, and W complexes,[1-3] that diazene ligands can be prepared from diazo ligands by reaction with protic acids,[3-6] and that diazene ligands in Rh and Pt complexes can be reduced under mild conditions using hydrogen in the presence of a catalyst[5,6] to form hydrazine ligands. These reactions suggest the possibility of reducing dinitrogen through this chemical route under mild conditions with the aid of transition metals. Indeed, Parshall and Sutton have suggested that aryldiazene complexes may be useful models for studying the reduction of dinitrogen in synthetic and biological systems.[6,7]

To date, the only other reported structure of a monodentate aryldiazene complex is that of $PtCl(p\text{-}HN_2C_6H_4F)(PEt_3)_2^+$.[8,9] In addition, two other iridium complexes have been studied which contain bidentate *trans*-aryldiazene ligands that have undergone ortho-metalation.[10,11] The ability of transition metals to stabilize through coordination otherwise unstable species is especially evident for aryldiazene complexes as well as for an interesting six-coordinate, rhenium complex which contains an another form (PhNH=N=Re) of phenyldiazene, $ReCl_2(N_2HPh)(NH_3)(PPhMe_2)_2^+$.[12] We now report the crystal structure of the six-coordinate, *cis*-phenyldiazene complex of ruthenium, $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4]$, and show that the aryldiazene ligand is conveniently identified using Raman vibrational and nuclear magnetic resonance spectroscopy.

## Experimental Section

**Crystal Preparation.** The title complex was prepared by two independent methods (eq 1, 2) which yielded identical products.

$$RuCl(CO)_2(N_2Ph)(PPh_3)_2 + HClO_4 \xrightarrow{EtOH} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4] \quad (1)$$

$$RuHCl(CO)_2(PPh_3)_2 + [PhN_2][ClO_4] \xrightarrow{Me_2CO} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][ClO_4] \quad (2)$$

The same complex as the $BF_4^-$ salt has been prepared by another method, eq 3.[5a] A reaction similar to eq 2 was performed using

$$[RuCl(CO)(HN_2Ph)(PPh_3)_3][BF_4] + CO \xrightarrow{Me_2CO} [RuCl(CO)_2(HN_2Ph)(PPh_3)_2][BF_4] + PPh_3 \quad (3)$$

$RuHCl(CO)_2(PPr_2Bu)_2$ as a starting material.[5b,8]

Raman, infrared, and NMR spectra show the cationic products to be the same in all three reactions. The yellow product prepared according to reaction 1 was recrystallized from acetone as poorly developed solvent-free crystals and from dichloromethane as beautiful, well-developed prisms of the 1:1 $CH_2Cl_2$ solvate which lost solvent at the rate of about 10% per day forming the unsolvated powder. At room temperature in the presence of air, the crystals are moderately photosensitive; they become completely black under ambient light conditions in about 2 days. In the absence of air or light, no decomposition was observed. Indeed, at −20° under