bonding sites in the Guo nucleus.

Future bonding studies with complex **1** will be concerned with nucleobases, nucleotides, and oligonucleotides and the role of steric effects in the ability of Cp*Rh to form terminal or intrastrand bonds with adenine or guanine oligomers.[2i,7] As well, the use of the Cp*Rh aqua complex, **1**, as an anchor for DNA molecules to various microscopy surfaces[15] and its biological activity[16] will also be reported in future publications.

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Supplementary Material Available: Listings of spectroscopic data and synthetic procedures for complexes **1–4** and $[Cp^*Rh(OTf)_2]_x$ and tables of crystal data, atomic coordinates, isotropic displacement coefficients, bond lengths, bond angles, and anisotropic displacement coefficients (9 pages); table of observed and calculated structure factors for **2** (8 pages). Ordering information is given on any current masthead page.

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Preference of *cis*-Amide Structure in *N*-Acyl-*N*-methylanilines

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The amide bond in *N*-methylbenzanilide (**1**, Chart I) is cis in the crystal and in solution, whereas that of benzanilide itself is trans.[1,2] The *cis*-amide preference in *N*-methylamides with two aromatic groups is general.[3,4]

The structures of four *N*-acyl-*N*-methylanilides with a non-aromatic group at the carbonyl end, i.e., isopropenyl (**2**), cyclopropyl (**3**), isopropyl (**4**), and *tert*-butyl (**5**), were examined by X-ray crystal analyses. It was proved that the molecules of all these compounds adopt the *cis*-amide structure in the crystal. The amide bonds were almost planar with torsion angles (C—N—C(=O)—C) of 5.0°, −1.2°, −1.4°, and 5.0° for **2**, **3**, **4**, and **5**, respectively, as were observed in ordinary amide compounds.[5] Overall molecular structures of these compounds, together with that of **1**, are illustrated by ORTEP drawings in Figure 1.

There were no significant differences in bond lengths and angles related to the amide bond among the four compounds **2–5**. The mean value of the amide C—N bond length was 1.354 Å, which is intermediate between the single-bond C—N length of 1.47 Å and the double-bond C=N length of 1.24 Å.[6] The summations of the three valence angles around the nitrogen were almost 360°,

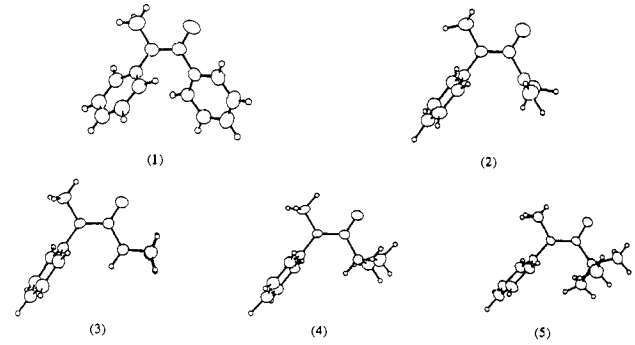
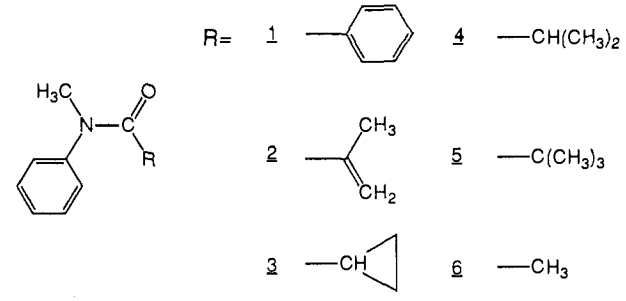


Figure 1. The ORTEP drawings of the molecules **1–5**.

Chart I



indicating the sp^2 character of the nitrogen atom. These facts suggest that the *N*-methyl amide bond in cis conformation retains partial double bond character similar to that of a free amide bond in trans conformation (1.34 Å in proteins and peptides and 1.376 Å in gaseous formamide[6]), and the hybridization nature of the amide nitrogen atom is not affected by N-methylation. On the other hand, interplanar angles between the phenyl ring and amide group were 60.0° for **1**, 96.9° for **2**, 84.2° for **3**, 78.2° for **4**, and 81.6° for **5**. The values indicate that the conjugation between imino nitrogen and the phenyl group has been lost in *N*-methylamides. Because the electronic stability gain of amide conjugation is more than that of anilide conjugation, the former conjugation was presumably realized at the cost of the latter conjugation to avoid severe steric hindrance between the phenyl ring and the aliphatic group at the carbonyl end. It seems to be of great interest that all of the compounds adopt *cis*-amide structures in spite of that disadvantage. It is obvious that there are no hydrogen-bonding networks to affect the molecular structures in these crystals, different from crystals of free amides. The results of NMR experiments supported the inherent preference of *cis*-amide structures to *trans*-amide in these compounds. Remarkable high-field signal shifts were observed for the C_β protons in the aliphatic groups of *N*-methylanilides, compared with those of the corresponding free anilides: 0.81 and 0.43 ppm for olefinic and 0.30 ppm for methyl protons in **2**, 0.24 ppm for cyclopropyl methylene protons in **3**, 0.23 ppm for protons of the two methyls in **4**, and 0.28 ppm for protons of the three methyls in **5**. These shifts are explained by the *cis*-amide structures, where the alkyl groups are located closely facing the phenyl ring plane.

Regarding the molecular structure of *N*-methylacetanilide (**6**)[7] in the crystal, it has been reported to be cis, in contrast to the trans structure in free acetanilide.[8] The NMR studies clearly supported the *cis*-amide preference in *N*-methylacetanilide in solution.[9]

Thus, it seems to be a general rule that *cis*-amide structure is preferred in *N*-methylamides with an aromatic group at the imino end and with any type of substituent group at the carbonyl end,

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regardless of its bulkiness or whether the group is aromatic or aliphatic.

It has been believed that amides usually exist in trans structures, as evidenced crystallographically in many proteins and peptides, although some peptides containing proline or N-methylated amino acid residues have cis structures, especially in cyclic peptides.[6] The change of conformational preference as a consequence of N-methylation is more distinct in anilide structures than in ordinary amides with an aliphatic group at the imino end. In order to investigate the cis preference of *N*-methylamides theoretically, extensive studies based on molecular orbital calculations are in progress.[10] Further generalization or extension of the applicability of this rule is also under investigation.

The amide group is very important in drug structures, not only from a synthetic viewpoint but also because of its chemical and physical properties. This paper raises the possibility that the *N*-methylamide moiety in anilides may be bioisostere of the cis carbon–carbon double bond.

Supplementary Material Available: Listing of crystal data, atom positioning and thermal parameters, and bond lengths and angles for compounds **2–5** (16 pages). Ordering information is given on any current masthead page.

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Reduced Derivatives of the Manganese Cluster in the Photosynthetic Oxygen-Evolving Complex

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Photosynthetic oxygen evolution requires Mn, Cl, and Ca and is believed to take place at a multinuclear Mn cluster (the oxygen-evolving complex, OEC).[1] Substantial effort has been devoted to elucidation of the cluster's structure using a variety of physical and chemical methods. We describe herein evidence from X-ray absorption spectroscopy that treatment in the dark with either hydroxylamine or hydroquinone results in substantial reduction of the Mn.

Treatment of photosystem II with micromolar concentrations of NH_2OH results in a two-flash delay in oxygen evolution.[2,3] Longer exposure time or millimolar concentrations of NH_2OH result in an eventual inhibitory loss of Mn(II).[4,5] The two-flash delay has been interpreted as arising from rapid reduction of Mn in the dark to a state formulated as S_{-1}.[6-9] This interpretation has been questioned most recently by Guiles et al.[10] They report, on the basis of X-ray absorption near edge structure (XANES), that NH_2OH does not cause reduction in the dark, but that reduction to a species formulated as S_0* *does* occur following illumination. Since it has recently been demonstrated[11] that millimolar concentrations of Ca^{2+} stabilize the OEC reaction center complex with respect to NH_2OH- and hydroquinone-induced loss of activity, we have used this stabilization technique to permit further study of reduced OEC derivatives using XANES.

Highly purified reaction center complex samples (specific activity = 1350 μmol of O_2 (mg of chlorophyll)$^{-1}$ h^{-1}) were prepared as previously described,[12] suspended at 0.67 mg of chlorophyll/mL, and dark adapted (>30 min at 4 °C) to prepare the OEC in the S_1 state.[13] This material was then either used directly (control) or treated with reductants (100 μM NH_2OH for 3 min or 200 μM hydroquinone for 30 min). Excess hydroxylamine was removed by 40-fold dilution. Ferricyanide was used to oxidize excess hydroquinone. A portion of each sample was diluted to 0.05 mg/mL chlorophyll and illuminated under saturated conditions for 3 min at 4 °C. As these illumination conditions allow multiple turnovers, the samples were again dark adapted for comparison with the S_1 control. Pellets of all samples were then packed into

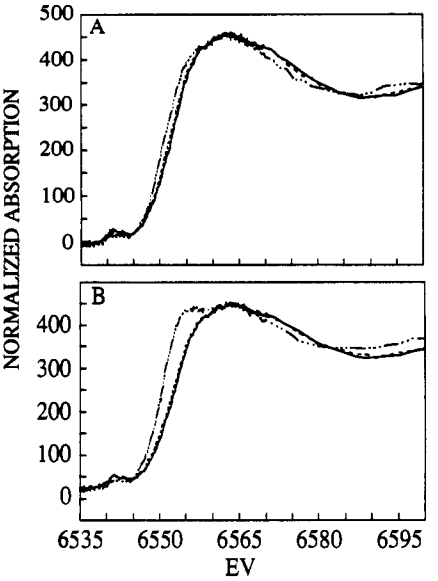

Figure 1. Normalized OEC XANES spectra: (—) S_1 control; (···) treated sample; (- - -) treated sample after illumination and dark adaptation. (A) NH_2OH-treated sample. (B) Hydroquinone-treated sample.

Table I. Manganese Oxidation State Composition for OEC[a]

sample	Mn(II)	Mn(III)	Mn(IV)
control (S_1)		49 (20)	51 (20)
hydroquinone	23 (7)	77 (7)	
	41 (5)		59 (5)
NH_2OH		86 (12)	14 (12)
	4 (5)	96 (5)	
	25 (7)		75 (7)

[a] Percent composition of different Mn oxidation states. Standard deviations (in parentheses) are for all combinations of models with the indicated oxidation states. For the reduced samples, several different oxidation-state models can be used to fit the data (see text).

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