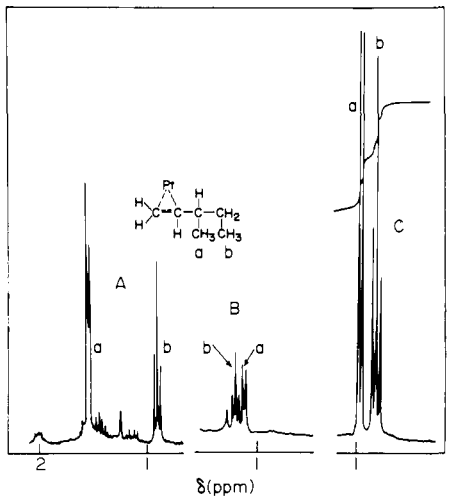


**Figure 2.** NMR spectra of complexed and uncomplexed 3-methylpent-1-ene. (A) 2*R*,3*S* diastereomer of the Pt complex II. The signal of the doublet at about 1.5 ppm contains a peak emanating from an impurity of the solvent. (B) 2*R*,3*R* diastereomer of the Pt complex II. (C) Uncomplexed 3-methylpent-1-ene.

of optically pure olefins and sulfoxides. Since in olefin resolution via Pt complexes one deals with a mixture of four diastereomers (olefins with one asymmetric center), the use of HPLC is obviously superior to that of crystallization.

Other important applications of the approach are in the field of metal-coordination chemistry, as manifest from the procedures used for the peak assignment of II. Even small amounts of the various stereoisomers, formed on complexation, can be detected. For unstable diastereomers, the purification of which by crystallization may not be possible,[14] HPLC offers an attractive route for the preparation of pure samples for NMR and chirooptical studies. Also, the relative stability of interconvertible isomers can be easily determined and the rate of epimerization measured.

Changes in the nature of the chiral *N*,*N*-dialkyl-α-amino acid coordinated to Pt makes available a variety of reagents with different stereoselective properties.[7] Such compounds could permit to widen the scope of the method to difficult problems of olefin and sulfoxide resolutions as well as extend it to additional classes of substances.

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**Registry No.** I, 80376-23-4; II[1], 80376-08-5; II[2], 80408-93-1; II[3], 80408-94-2; II[4], 80408-95-3; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*R*-methylphenyl sulfoxide)Pt[II], 80376-41-6; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylgycine)(*S*-methylphenyl sulfoxide)Pt[II], 80409-00-3; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*R*-methyl(4-methylphenyl) sulfoxide)Pt[II], 80376-38-1; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*S*-methyl(4-methylphenyl) sulfoxide)Pt[II], 80408-99-7; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*R*-methyl(4-*tert*-butylphenyl) sulfoxide)Pt[II], 80376-39-2; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*S*-methyl(4-*tert*-butylphenyl) sulfoxide)Pt[II], 80408-98-6; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*R*-methyl(4-bromophenyl) sulfoxide)Pt[II], 80433-06-3; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*S*-methyl(4-bromophenyl) sulfoxide)Pt[II], 80376-42-7; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*R*-phenyl(4-methylphenyl) sulfoxide)Pt[II], 80376-40-5; *trans*-chloro(*N*,*N*-dimethyl-*D*-phenylglycine)(*S*-phenyl(4-methylphenyl) sulfoxide)Pt[II], 80408-97-5; 3-methylhex-1-ene, 3404-61-3; 2,3-dimethylhex-1-ene, 16746-86-4; 4-methylcyclohexene, 591-47-9; 3,5,5-trimethylcyclohexene, 933-12-0.

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## A New Role for Hydrogen-Bond Acceptors in Influencing Packing Patterns of Carboxylic Acids and Amides

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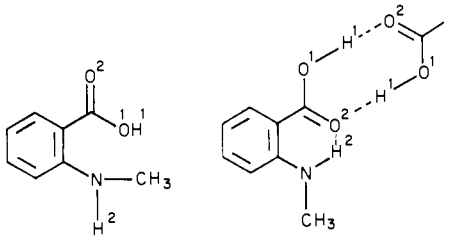
Several criteria for predicting the hydrogen-bonding patterns in carboxylic acids and amides previously have been proposed on the basis of lattice energy calculations[1] and analysis of the structures of many kinds of amides and acids.[2-4] Two of these criteria have proven particularly useful: (1) The crystal structure of an acid or amide will form in such a way that the maximum number of hydrogens which could possibly form H bonds will in fact form such bonds. (2) Certain H-bonding patterns have special significance because they are observed to occur so frequently. Among these are the cyclic H-bonded dimer pattern, the doubly H-bonded carbonyl groups, and the intramolecular H bond which occurs between ortho substituents on aromatic rings. In our studies of solid-state rearrangements of derivatives of anthranilic acid and related compounds[5] we have found that an additional principle appears to be operating: (3) The crystal structure of an acid or amide will form in such a way that the maximum number of hydrogen acceptor sites will be involved in H bonding.

This concept is best illustrated by considering the structures of acids or amides in which there are more hydrogen acceptor sites than hydrogens available for forming H bonds. In these cases the hydrogen atoms have a choice about both how many and which acceptor sites to use in forming hydrogen bonds. A clear example of this is seen by comparing the structures of *N*-methylanthranilic acid (I)[6] and *N*-acetylanthranilic acid (II).[7] Compound II has more acceptor sites than hydrogens (3:2), while I has an equal number. In the structure of I, shown below, its two hydrogens



I

are involved in the usual intramolecular and cyclic dimer H-bond arrangements referred to above. There are no other acceptor sites present. Addition of an extra acceptor at the methyl position of I need not interfere with the H-bonding scheme of I, but a significant change in the packing pattern is observed. The cyclic dimer pattern has been replaced by a polymeric-like pattern incorporating the acetyl group (O3–H1), resulting in a structure which satisfies criterion 3. Another indication that this structure represents the maximum use of its hydrogen acceptor sites is that

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(7) We solved the structure of this compound inadvertently when we collected data on crystals of acetylanthranyl recrystallized from water. We thought we had grown the hydrated form of acetylanthranyl but the water had actually reacted with this compound to form I. We discovered the error when we used the CIS crystallography data base to retrieve all known structures with space group *Fdd2* and found that compound I was in this space group and had the same unit cell parameters as our crystal. The structure of I can be found in Y. P. Mascarenhas, V. N. deAlmeida, J. R. Lachat, and N. Barelli, *Acta Crystallogr. Sect. B*, **B36**, 502 (1980).
(8) L. Leiserowitz and F. Nader, *Acta Crystallogr., Sect. B*, **B33**, 2719 (1977).

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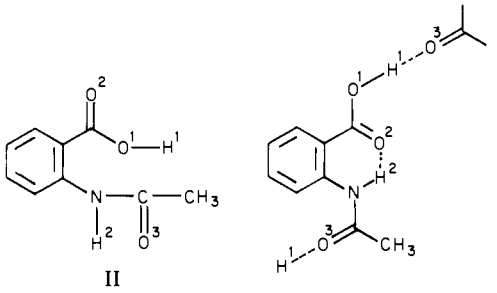
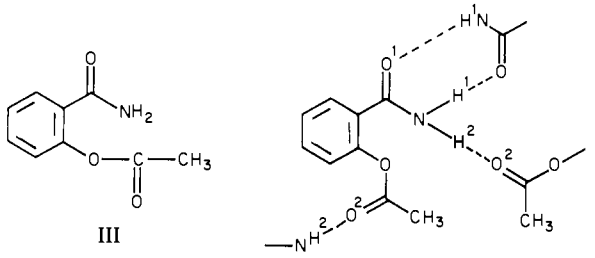


II

there are no doubly hydrogen-bonded oxygens present.

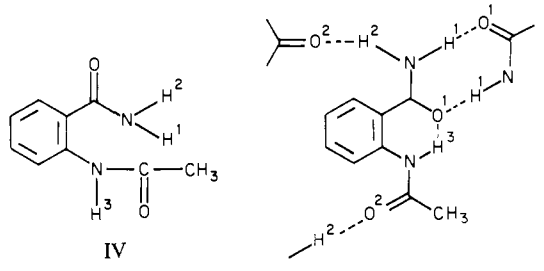
The structure of II could also be accounted for on the basis that amide oxygens are stronger proton acceptors than carboxyl oxygens, so one would expect H1 to bond to O3. In the structure of O-acetylsalicylamide (III), however, the ester carbonyl is linked



III

to an amide hydrogen,[9] consistent with criterion 3 but yet contrary to the expected hydrogen acceptor strengths of the two carbonyl groups in this compound. In benzamide, and in many other primary amides, the amide carbonyl bonds to both H1 and H2.[10] It may be that the important point here is *not* that the weaker acceptor was used but that relative acceptor strengths derived from solution experiments do not necessarily correlate with the bonding characteristics of these functional groups in the solid state.

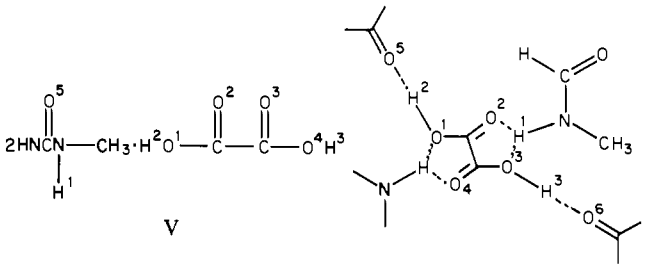
In a related example, which we reported recently[5] there are two polymorphs of *N*-acetylanthranilamide (IV), both of which have hydrogen bonds to all the avilable hydrogen acceptors. Since there are more hydrogens than acceptor sites in these structures (3:2), it is not surprising that they both contain cyclic dimer H-bond patterns. The $\alpha$ form of IV has the H-bonding features of both I and II in that there is an intramolecular H bond in addition to the cyclic dimer (like I) and also a hydrogen bond to the acetyl carbonyl (H2–O2) like II. Upon heating, this polymorph rearranges in such a way that all the acceptor sites remain H bonded even though the intramolecular H bond is broken, suggesting that criterion 3 may supercede 2 in importance in this case.



IV

An intriguing example which supports this new packing criterion is that of the structure of the 2:1 adduct of *N*-methylformamide with oxalic acid (V).[8] In this complex there are six acceptor sites and only four available hydrogens. The H-bonding pattern found has the oxalic acid hydrogens bonded to the two formamide oxygens (H2, H3–O5, O6). This leaves only two hydrogens to bond to the remaining four oxygens of the acid. In order to involve all of the oxygens the formamide hydrogen becomes bifurcated.

From a literature survey of approximately 50 structures which contain only amide and/or acid groups, we have found that



V

criterion 3 is satisified in all but two structures. In addition, all structures surveyed which contain phenol oxygens or amine nitrogens in addition to the acid and amide groups have hydrogen-bonding networks which incorporate the phenol and amines as hydrogen-bond acceptors also. On the other hand, groups like esters, nitro groups, sulfones, sulfonic acids, and furans while capable of forming hydrogen bonds are not always used as acceptor sites for hydrogen bonding.

As seen by structures II–IV, one result of incorporating the maximum number of acceptor sites into the H-bonding schemes is that extended polymer-like chains and networks are formed. We are interested in seeing whether or not there is evidence that these chains form in solution as well as in solid state. In addition, we are pursuing the possibility that solid–gas reactions of acids and amides with water vapor may be related to whether or not there are "free" hydrogen acceptor sites in the crystal. Indeed this may play a part in whether or not crystalline hydrates of amides and acids can be grown from solution.

**Registry No.** I, 119-68-6; II, 89-52-1; III, 5663-71-8; IV, 33809-77-7; V, 80399-20-8.

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## Retention of Configuration during Ligand-Substitution Reactions of Cyclopentadienylrhodium Complexes Containing an Acyl Ligand

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There is considerable interest in the stereochemical fate of chiral centers in organometallic complexes during simple reactions. These centers can be either chiral ligands or complexes where the optical activity is due to asymmetry at the metal atom. Pseudotetrahedral complexes of the type CpMLL'L'' are examples of the latter whose preparation and resolution has been studied extensively by Brunner[2] and co-workers. The stereochemical fate of an optical center is a powerful mechanistic probe. Specific studies of the stereochemistry at the metal have been reported for reactions such as the photochemical decarbonylation of acyl ligands,[3] the insertion of $SO_2$ into iron–carbon bonds,[4] electrophilic cleavage of the latter,[5] asymmetric induction,[6] and ligand sub-

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