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FORMATION OF A CRYSTALLINE MOLECULAR COMPLEX BETWEEN A CHIRAL SULFOXIDE AND A CHIRAL AMIDE

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Abstract

(R)-methyl p-tolyl sulfoxide 2 and (S)-N-(3,5-dinitrobenzoyl)-1-phenyl ethylamine 1 give a crystalline 1:1 molecular complex. The crystal structure of this complex is studied in detail. Existence of hydrogen bond between S=O and NH could be established. Its importance in the use of (S) or (R)-1 as a chiral solvating agent for nmr determination of ee of sulfoxides is briefly discussed.

During the course of our studies on asymmetric oxidation of sulfides[1,2] we used some chiral amides as solvating agents for the measurement of the enantiomeric purity of sulfoxides by nmr[3]. Most of the experiments were performed with amide 1. Recently Pirkle et al. have reported the use of 3,5-dinitrobenzoyl amino acid esters for the nmr determination of ee of many types of solutes[4]. We wish to report the isolation and characterization of a 1:1 complex between (S)-1 and sulfoxide (R)-2. The molecular complex was obtained by crystallization[5]. The crystal structure was solved using direct methods (MULTAN[8]) and the Patterson heavy-atom method as well. A few selected bond lengths and angles are indicated in Table 1, and a partial packing of the complex is shown.It appears from the crystal structure that one molecule of 1 is hydrogen bonded through NH to the S=O group of 2 (N(3)-O(1)=2.85(2)Å).

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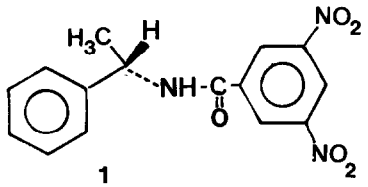

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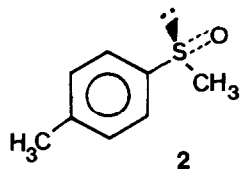


2

Planes π(1) and π(3) within an adduct are almost parallel whereas plane π(2) is almost perpendicular to π(1) and π(3). Planes π(1) and π(3) from different molecules are almost parallel to each other with distances between the centroids of π(1) and π(3) of 3.84 Å and 4.02 Å giving a period close to $\vec{a}$: indeed the stacking of these phenyl planes is along $\vec{a}$. Such rather small distances between parallel phenyl groups observed in the solid state bring an argument in favour of an additional intermolecular interaction between these groups in solution, which appears to be a charge transfer between 1 and 2.

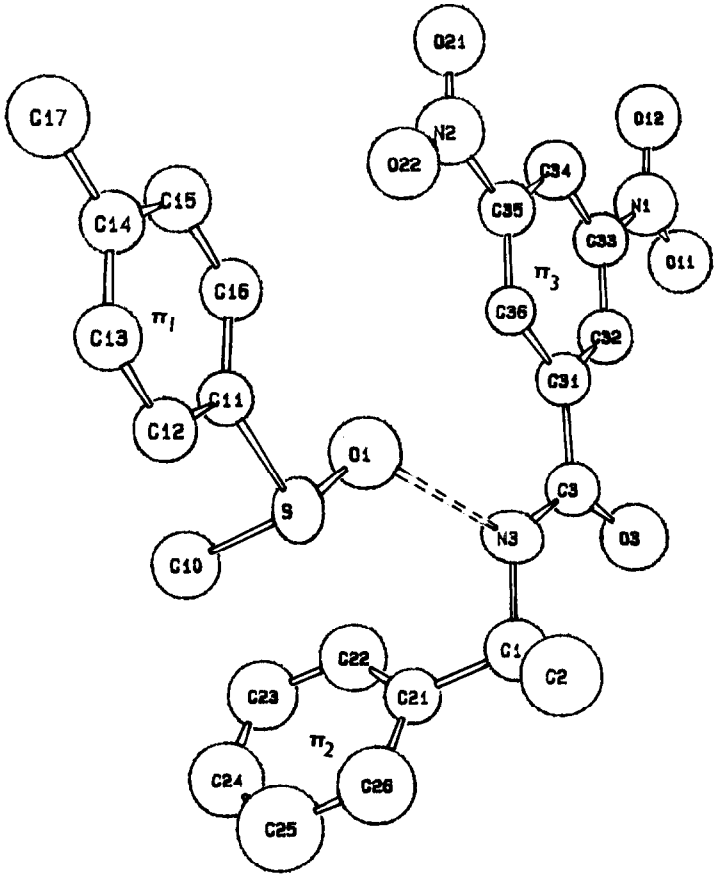
This structure illustrates one of the few examples of molecular complexes between a chiral sulfoxide and a chiral partner. The most recent example is the crystal structure of 1:1 complex between 2 and 1,1'-(binaphthol-2)[9].

We assumed[3] that the successful utilization of 1 as chiral solvating agent of sulfoxides was primarily based on the formation of weak complexes involving an hydrogen bond betwen sulfoxides and an acidic NH. The isolation of the molecular complex (S)-1/(R)-2 gives some support to this hypothesis and suggests a potential use of 1 as resolving agent for sulfoxides. We are presently investigating this area.

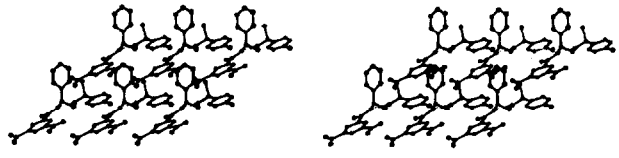
TABLE 1

Selected bond distances (Å) and angles (°)

C(1) - C(2)	: 1.52(2)	S - O(1)	: 1.462(8)
C(1) - C(21)	: 1.485(15)	S - C(10)	: 1.736(11)
C(1) - N(3)	: 1.449(14)	S - C(11)	: 1.806(10)
N(3) - C(3)	: 1.353(13)	C(10) - S - O(1)	: 108.0(5)
C(3) - O(3)	: 1.247(14)	C(10) - S - C(11)	: 98.9(5)
C(3) - C(31)	: 1.448(14)	O(1) - S - C(11)	: 105.5(5)



Representation of the 1:1 complex showing the S=O···HN hydrogen bond.



Crystal packing

Acknowledgments

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References and notes

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(5) Amide (S)-1,$[\alpha]_D$ = + 48.8°C (c=1, acetone), crystallization in methanol, mp : 154°C and 159°C.
Sulfoxide (R)-2, $[\alpha]_D$ = +142.6°C (c=1, acetone), crystallization in hexane, mp 75°C.
31.5 mg (0.1 mmol) of (S)-1 and 15.9 mg (0.1 mmol) of (R)-2 were dissolved in 2 mL of cyclohexane:ethyl acetate (1:1). A slow evaporation of solvent allowed the formation of long colorless needles[6], mp : 130°C.$[\alpha]_D$ = + 75.7°C (c=0.2, acetone).

(6) Analysis : $C_{23}H_{23}N_3O_8S$ = 469.52
Calc. % : C = 58.84 H = 4.94 N = 8.95 O = 20.45 S = 6.83
Found % : C = 58.84 H = 4.91 N = 8.88 O = 20.47 S = 6.83.

(7) Crystal data : monoclinic, space group $P2_1$, a = 7.808(3), b = 6.848(7), c = 21.945(9), β = 98.34(3), V = 1161(2) Å^3, Z = 2, D_x = 1.343 Mg m^{-3}.
Final R factor = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ = 0.064 and weighted WR factor = 0.066 (unit weights) were obtained after refinement for 1466 unique reflections.

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