

Crystal and molecular structure of Rebek's imide

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Received May 15, 2003

The crystal and molecular structure of Rebek's imide **1** is reported. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 7.8733(7)$ Å, $b = 12.712(1)$ Å, $c = 12.789(1)$ Å, $\alpha = 86.628(5)^\circ$, $\beta = 84.628(5)^\circ$, $\gamma = 72.981(5)^\circ$, $V = 1217.9(2)$ Å³, and $D_c = 1.305$ g/cm³ for $Z = 2$ and $R = 0.047$. The molecule crystallizes as a cyclic, hydrogen-bonded dimer held together by two N—H···O and two O—H···O hydrogen bonds involving amide···carboxylic acid interactions. The dimer organizes in the solid state to form 1D ribbons.

KEY WORDS: Imide; hydrogen-bonding; carboxylic acid; dimer.

Introduction

Rebek's imide **1**,¹ a derivative of Kemp's triacid,² was developed in the mid-1980s as a platform for studies in molecular recognition. Derivatives of **1** have been used, for example, as model receptors for adenine derivatives,³ as templates to direct reactivity,⁴ and as receptacles to study acid–base interactions.⁵ Such studies have, in part, been achieved owing to a ready ability to functionalize the cleft-shaped molecule with convergent functional groups able to participate in hydrogen bonding, π - π interactions, and coordination bonds.¹

Although a large number of derivatives of Rebek's imide have been reported, we were surprised to discover that **1** has not been crystallographically characterized. In this paper, we report the crystal and molecular structure of **1**.

Experimental

Synthesis

All reagents were purchased from Aldrich Chemical Co. and were used as received, unless otherwise stated. **1** was prepared according to the literature.⁶ Single-crystals of **1** suitable for X-ray analysis were obtained by slowly cooling a warm aqueous solution of **1** to room temperature and letting the solution stand for a period of approximately 1 day.

X-ray crystallography

A single crystal of **1** was mounted on the end of a glass fiber and optically centered in the X-ray beam of a Nonius Kappa system for data collection. Cell constants were calculated from reflections obtained from the data collection. The structure was solved using direct methods. After anisotropic refinement of all non-hydrogen atoms, methylene, methyl, hydroxyl, and amide hydrogen atoms were placed in idealized positions

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Table 1. Crystal Data and Structure Refinement for **1**

CCDC deposit no.	210453
Empirical formula	C ₂₄ H ₃₄ N ₂ O ₈
Formula weight	478.5
Crystal size	0.25 × 0.30 × 0.34
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>T</i> (°C)	−83
θ range for data collection (°)	2 ≤ θ ≤ 22.5
<i>a</i> (Å)	7.8733(7)
<i>b</i> (Å)	12.712(1)
<i>c</i> (Å)	12.789(1)
α (°)	86.628(5)
β (°)	84.628(5)
γ (°)	72.981(5)
<i>V</i> (Å ³)	1217.9(2)
<i>Z</i>	2
ρ_{calc} , g cm ^{−3}	1.305
μ , mm ^{−1}	0.0979
No. of measured reflections	6079
No. of unique reflections	3187
No. of observed reflections ^a	2429
<i>R</i> _{merge}	0.029
<i>R</i> ^a	0.0472
<i>wR</i> ²	0.1605

^a*I* > 2 σ (*I*).

and allowed to ride on the atom to which they are attached. A summary of data collection parameters is given in Table 1. Structure solution was accomplished with the aid of SHELXS-86⁷ and refinement was conducted using SHELXL93⁸ locally implemented on a Pentium-based IBM compatible computer. All crystallographic manipulations were performed with the aid of RES2INS.⁹

Results and discussion

Final positional coordinates and interatomic bond distances and angles are given in Tables 2 and 3, respectively.

An ORTEP perspective of **1** is shown in Fig. 1. The asymmetric unit contains two full molecules of **1** (molecules A and B). Each molecule self-assembles to form a discrete hydrogen-bonded dimer, which sits around a crystallographic center of inversion, held together by N—H...O and O—H...O hydrogen bonds. The

Table 2. Final Fractional Positional Coordinates and *U*_{eq} (10^{−4} Å²) for **1**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^a
O1	0.1600(2)	0.0628(2)	−0.5521(2)	353(8)
O2	0.3338(3)	−0.0659(2)	−0.2323(2)	430(8)
O3	0.4838(2)	0.1550(2)	−0.4990(2)	341(7)
O4	0.5706(2)	0.0869(2)	−0.3410(2)	362(7)
N1	0.2420(3)	0.0055(2)	−0.3898(2)	299(9)
C1	0.1464(3)	0.0825(2)	−0.4581(2)	291(10)
C2	0.0308(3)	0.1897(2)	−0.4120(2)	314(11)
C3	−0.0303(3)	0.1674(2)	−0.2979(2)	326(11)
C4	0.1297(4)	0.1184(2)	−0.2328(2)	299(11)
C5	0.2419(4)	0.0118(2)	−0.2816(2)	319(12)
C6	0.2457(4)	0.1991(2)	−0.2361(2)	321(10)
C7	0.3029(4)	0.2386(2)	−0.3465(2)	308(10)
C8	0.1433(3)	0.2719(2)	−0.4145(2)	316(11)
C9	0.4596(3)	0.1548(2)	−0.4036(2)	291(11)
C10	−0.1271(4)	0.2389(3)	−0.4779(3)	411(12)
C11	0.0722(4)	0.0951(3)	−0.1187(2)	390(11)
C12	0.3722(4)	0.3386(3)	−0.3363(3)	403(11)
O5	0.8133(3)	−0.5672(2)	−0.2327(2)	476(9)
O6	0.6707(3)	−0.4239(2)	0.0880(2)	380(8)
O7	1.0713(3)	−0.4208(2)	−0.1835(2)	403(8)
O8	1.0037(3)	−0.3438(2)	−0.0266(2)	377(7)
N2	0.7394(3)	−0.4880(2)	−0.0759(2)	323(9)
C13	0.7324(4)	−0.4854(3)	−0.1847(2)	354(11)
C14	0.6259(4)	−0.3788(3)	−0.2340(2)	374(12)
C15	0.4726(4)	−0.3235(3)	−0.1546(2)	387(11)
C16	0.5421(4)	−0.2994(2)	−0.0533(2)	348(11)
C17	0.6534(4)	−0.4072(2)	−0.0072(2)	313(11)
C18	0.6609(4)	−0.2223(2)	−0.0806(2)	327(11)
C19	0.8146(4)	−0.2626(2)	−0.1650(2)	335(11)
C20	0.7473(4)	−0.3029(3)	−0.2597(2)	386(12)
C21	0.9699(4)	−0.3472(2)	−0.1169(2)	312(11)
C22	0.5570(5)	−0.4020(3)	−0.3354(3)	520(14)
C23	0.3889(4)	−0.2441(3)	0.0270(3)	457(14)
C24	0.8897(4)	−0.1652(3)	−0.2007(3)	447(12)

^a*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

imide function and carboxylic acid group participate in amide...carboxylic acid interactions, forming seven-membered rings composed of two N—H...O [N...O separations (Å) 2.834(3) (A), 2.831(3) (B)] and two O—H...O [O...O separations (Å) 2.718(2) (A), 2.711(3) (B)] forces (Esters of Rebek's imide self-assemble via hydrogen bonds to form dimers involving amide...amide interactions [see, also: ref.³]). As a consequence of the assembly process, the hydrogen bond functionalities are situated at the center of the complex, while the methyl groups

Table 3. Interatomic Distances (Å) and Angles [°] for **1**

Bonds			
O1—C1	1.231(4)	O5—C13	1.216(4)
O2—C5	1.221(3)	O6—C17	1.236(4)
O3—C9	1.216(4)	O8—C21	1.216(4)
O4—C9	1.326(3)	O7—C21	1.330(3)
N1—C1	1.371(3)	N2—C13	1.396(4)
N1—C5	1.391(4)	N2—C17	1.368(4)
C1—C2	1.517(4)	C13—C14	1.506(4)
C2—C3	1.530(4)	C14—C15	1.529(4)
C2—C8	1.553(5)	C14—C20	1.548(5)
C2—C10	1.525(4)	C14—C22	1.528(5)
C3—C4	1.531(4)	C15—C16	1.533(5)
C4—C5	1.517(4)	C16—C17	1.514(4)
C4—C6	1.557(5)	C16—C18	1.547(5)
C4—C11	1.526(4)	C16—C23	1.536(4)
C6—C7	1.542(4)	C18—C19	1.533(4)
C7—C8	1.538(4)	C19—C20	1.537(5)
C7—C9	1.532(4)	C19—C21	1.524(4)
C7—C12	1.539(5)	C19—C24	1.549(5)
Angles			
H4O—O4—C9	109.5(2)	H7O—O7—C21	109.5(2)
H1N—N1—C1	116.1(2)	H2N—N2—C13	116.0(2)
H1N—N1—C5	116.1(2)	H2N—N2—C17	116.1(3)
C1—N1—C5	127.8(2)	C13—N2—C17	127.9(3)
O1—C1—N1	119.4(3)	O5—C13—N2	118.6(3)
O1—C1—C2	123.7(3)	O5—C13—C14	124.9(3)
N1—C1—C2	116.9(2)	N2—C13—C14	116.5(3)
C1—C2—C3	108.9(2)	C13—C14—C15	108.2(3)
C1—C2—C8	108.8(2)	C13—C14—C20	109.1(3)
C1—C2—C10	109.7(2)	C13—C14—C22	109.6(3)
C3—C2—C8	109.1(2)	C15—C14—C20	109.3(3)
C3—C2—C10	111.6(2)	C15—C14—C22	111.4(3)
C8—C2—C10	108.7(2)	C20—C14—C22	109.2(3)
C2—C3—C4	110.9(2)	C14—C15—C16	111.3(3)
C3—C4—C5	108.3(2)	C15—C16—C17	108.2(2)
C3—C4—C6	109.8(2)	C15—C16—C18	108.8(2)
C3—C4—C11	111.9(2)	C15—C16—C23	111.7(3)
C5—C4—C6	108.4(2)	C17—C16—C18	109.2(2)
C5—C4—C11	109.3(2)	C17—C16—C23	109.9(2)
C6—C4—C11	109.1(2)	C18—C16—C23	109.1(2)
O2—C5—N1	119.1(3)	O6—C17—N2	119.7(3)
O2—C5—C4	124.1(3)	O6—C17—C16	123.1(3)
N1—C5—C4	116.8(2)	N2—C17—C16	117.2(3)
C4—C6—C7	115.9(2)	C16—C18—C19	115.7(2)
C6—C7—C8	110.1(2)	C18—C19—C20	110.1(2)
C6—C7—C9	114.2(2)	C18—C19—C21	110.0(2)
C6—C7—C12	109.2(2)	C18—C19—C24	108.3(2)
C8—C7—C9	109.8(2)	C20—C19—C21	114.5(3)
C8—C7—C12	109.3(2)	C20—C19—C24	109.5(3)
C9—C7—C12	104.1(2)	C21—C19—C24	104.2(2)
C2—C8—C7	115.8(2)	C14—C20—C19	116.1(3)
O3—C9—O4	123.2(3)	O7—C21—O8	122.8(3)
O3—C9—C7	122.0(3)	O7—C21—C19	114.5(2)
O4—C9—C7	114.7(2)	O8—C21—C19	122.6(3)

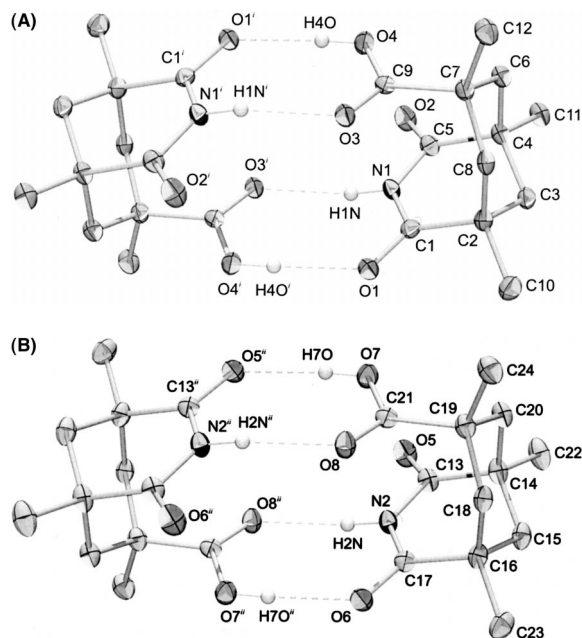


Fig. 1. ORTEP perspectives of **1**: (a) molecule A and (b) molecule B. Thermal ellipsoids of non-hydrogen atoms are given at 30% probability level. Selected interatomic distances (Å) and angles (°): O(4)⋯O(1)ⁱ = 2.718(2), O(4)—H(4O) = 0.840, H(4O)⋯O(1)ⁱ = 1.886(2), O(4)—H(4O)—O(1)ⁱ = 170.2(2), N(1)⋯O(3)^j = 2.834(3), N(1)—H(1N) = 0.880, H(1N)⋯O(3)^j = 1.993(2), N(1)—H(1N)—O(3)^j = 159.6(2), O(7)⋯O(6)ⁱⁱ = 2.711(3), O(7)—H(7O) = 0.840, H(7O)⋯O(6)ⁱⁱ = 1.880(2), O(7)—H(7O)—O(6)ⁱⁱ = 169.9(2), N(2)⋯O(8)ⁱⁱ = 2.831(3), N(2)—H(2N) = 0.880, H(2N)⋯O(8)ⁱⁱ = 1.977(2), N(2)—H(2N)—O(8)ⁱⁱ = 163.4(2). Symmetry operators: *i*: $-x + 1, -y, -z - 1$; *ii*: $-x + 2, -y - 1, -z$.

are located along the periphery of the assembly. Notably, the imide function of each molecule is approximately planar, the largest deviation of the imide atoms being 0.015 Å and 0.027 Å for nitrogen atoms in molecules A and B, respectively. Bond lengths [distances (Å): C=O 1.216(4) (A), 1.216(4) (B); C—O 1.326(3) (A), 1.330(3) (B)] and angles [angles (°): O—C—O 123.2(3) (A), 122.8(3) (B)] of the carboxyl groups are consistent with **1** being in the acid form.¹⁰

A view of the extended structure of **1** is shown in Fig. 2. The hydrogen-bonded dimers assemble in the solid state to form 1D ribbons.

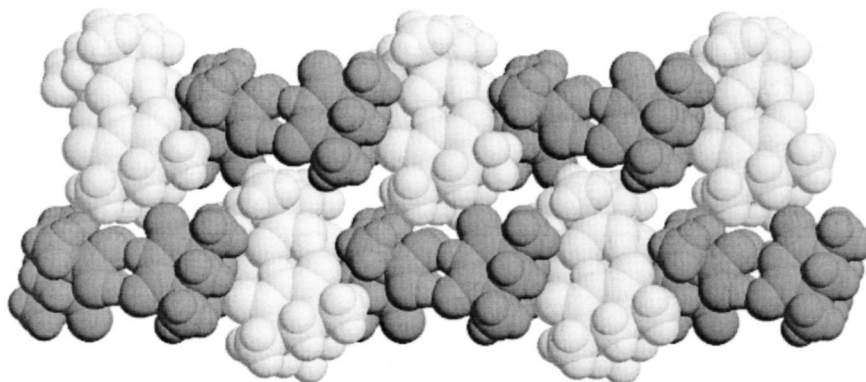


Fig. 2. Space-filling view of the extended structure of **1** (molecules A and B shown in gray and black, respectively).

Each ribbon is composed of dimers oriented in a perpendicular fashion, wherein the methyl groups of each complex exhibit a “tongue-in-groove” fit with the imide and carboxylic acid functionality. Adjacent ribbons stack offset, along the crystallographic *a*-axis, such that the methyl groups are located above and below the hydrogen bonds.

Acknowledgments

We are grateful for support from the University of Iowa and the National Science Foundation (CAREER Award, DMR-0133138, L.R.M.).

References

1. Rebek, J. *Angew. Chem., Int. Ed.* **1990**, *102*, 261.
2. Kemp, D.S.; Petrakis, K.S. *J. Org. Chem.* **1981**, *46*, 5140.
3. Castellano, R.K.; Gramlich, V.; Diederich, F. *Chem. Eur. J.* **2002**, *8*, 118.
4. Pieters, R.J.; Huv, I.; Rebek, J. *Tetrahedron* **1995**, *51*, 485.
5. Wash, P.L.; Renslo, A.R.; Rebek, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1221.
6. Rebek, J.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476.
7. Sheldrick, G.M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
8. Sheldrick, G.M. *SHELXL93*, University of Göttingen: Germany, 1993.
9. Barbour, L.J. *RES2INS*, Program for Graphic Representation of *SHELXL* Instruction Files, University of Missouri-Columbia, Missouri, USA. **1997**.
10. Ichikawa, M. *J. Cryst. Mol. Struct.* **1979**, *9*, 87.