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THE STRUCTURE OF TETRAKETONES IN THE SOLID STATE: THE CRYSTAL STRUCTURE OF 1,6-DIPHENYLHEXANE-1,3,4,6-TETRONE

By

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تركيب رباعي الكيتون في الحالة الصلبة : التركيب البلوري لمركب ١ , ٦ - ثنائي الفينيل هكسان - ١ , ٣ , ٤ , ٦ - تترون

نجوى نوار

تم في السنوات الأخيرة تحديد الشكل البلوري المتناظر لمركب ١ , ٥ - ثنائي فينيل ١ , ٣ , ٥ ثلاثي الكيتون عبر الأبحاث السابقة . كما درست مركبات رباعي الكيتون بواسطة الرنين النووي المغناطيسي NMR وطيف الأشعة تحت الحمراء IR وطيف الكتلة . وقد تبين أنها توجد في حالة إتزان بين الشكلين الكيتوني والأنيولي ويميل بصوره أكبر إلى الشكل الآنيولي .

وفي هذا البحث تم تحديد البنيه البلوريه للمركب ١ , ٦ ثنائي فينيل البنتان ١، ٣ ، ٤، ٦ رباعي ، والذي يوجد بالشكل الثنائي الاينول .

Key Words: 1,6-Diphenylhexane-1,3,4,6-tetrone, Crystal ttructure

ABSTRACT

The crystal structure of 1,6-diphenylhexane-1,3,4,6-tetrone was determined, $C_{18}H_{14}O_4$, M 294.31 monoclinic, space group $P2_1/n$ (# 14), α 5.1192 (6) Å, b 9.085 (9) Å, c 15.366 (4) Å, b 97.91 (4)°, ρ (calc) 1.362 g/cm3, Z 2, F(000) 308, μ (Mo K α)3 0.90cm^{-1}. The structure was solved by direct methods and refined to a final R value of 0.045 for 1364 unique reflections. The molecules of the compound are found in the dienol form.

INTRODUCTION

1,3,5-triketones are potentially dinegative, tridentate ligands and metal complexes of them have been prepared with transition metals[1-3], lanthanides[4] and actinide[5] ions. The crystal structure of the symmetric triketone, 1,5-diphenylpentane-1,3,5-trione has been determined[6].

To our knowledge no crystal structures of the 1,3,4,6-tetraketones have been reported. The NMR, IR and mass spectra for the compounds of tetraketones show that in the keto-enol tautomeric equilibrium the enol form largely predominates[7]. The chelated hydrogen bonded enol form is the reactive one, giving complexes with a variety of metal ions[8].

In the course of our studies on the synthesis and properties of polyoxo complexes, we had an opportunity to investigate the crystal structure of the symmetric tetraketone, 1.6-diphenylhexane-1,3,4,6-tetrone, in order to ascertain the nature of the compound in the crystalline state.

Crystal data

The crystal used had dimensions of 0.200 x 0.400 mm; $C_{18}H_{14}O_4$, M 294.31 monoclinic, space group $P2_1/n$ (# 14), a 5.192 (6), b 9.085 (9), c 15.366 (4) Å, β 97.91 (4)°, ρ (calc) 1.362 g/cm^3, Z 2, μ (Mo Kα) 0.90 cm^{-1}, F(000) 308.

Data collection and structure solution and refinement:

A yellow prism crystal of $C_{18}H_{14}O_4$ having approximate dimensions of 0.200 x 0.200 x 0.400 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, was obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range $20.08 < 2\theta < 37.41°$.

The data were collected at 23 ± 1°C of the 1521 reflections which were collected, 1364 were unique (R_{int} = 0.038) and no decay correction was applied.

The linear absorption coefficient for Mo Kα is 0.9 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.97 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[9]. Full-matrix least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, reduced R to 0.045 and R_W 0.041. The hydrogen atom H(6) bonded to the oxygen atom was located from a difference map and refined freely while the remaining hydrogen atoms were placed in idealized positions.

DISCUSSION

The crystal consists of discrete molecules with a diketo-dienol structure as shown in Fig. (1). Intramolecular hydrogen bonds occur between the terminal ketone oxygen atoms 0(1) and the hydrogen atoms of the enol groups with 0(1) ...H(6) [1.50 (7) Å].

Table 1
Positional parameters for Tetrone

Atom	X	Y	Z
O(1)	1.0768 (7)	0.2127 (4)	0.5324 (2)
O(2)	1.4602 (7)	0.3715 (4)	0.5830 (2)
C(1)	0.821 (1)	0.2351 (6)	0.3940 (3)
C(2)	0.751 (1)	0.3092 (6)	0.3153 (3)
C(3)	0.539 (1)	0.2627 (8)	0.2570 (3)
C(4)	0.395 (1)	0.1435 (8)	0.2771 (4)
C(5)	0.463 (1)	0.0680 (6)	0.3545 (4)
C(6)	0.675 (1)	0.1133 (6)	0.4124 (4)
C(7)	1.043 (1)	0.2822 (6)	0.4604 (3)
C(9)	1.209 (1)	0.4004 (6)	0.4449 (3)
C(10)	1.410 (1)	0.4389 (6)	0.5065 (3)
H(6)	1.300 (1)	0.2920 (8)	0.5830 (4)

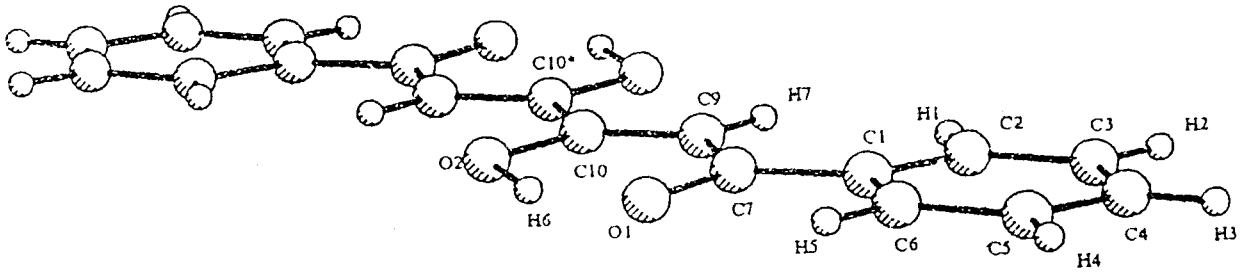


Fig. 1 Molecular structure showing atom labelling

Table 2
Bond lengths (Å) and Angles (°) for Tetrone.

Atom	Atom	Distance	Atom	Atom	Distance
O (1)	C (7)	1.266 (5)	C (3)	C (4)	1.375 (8)
O (2)	C (10)	1.318 (5)	C (4)	C (5)	1.376 (8)
O (2)	H (6)	1.09 (7)	C (5)	C (6)	1.378 (7)
C (1)	C (2)	1.388 (7)	C (7)	C (9)	1.420 (7)
C (1)	C (6)	1.390 (7)	C (9)	C (10)	1.355 (6)
C (1)	C (7)	1.493 (6)	C (10)	C (10)	1.48 (1)
C (2)	C (3)	1.386 (7)	O (1)	H (6)	1.50 (7)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C (10)	O (2)	H (6)	105 (3)	C (1)	C (6)	C (5)	120.9 (5)
C (2)	C (1)	C (6)	118.7 (5)	O (1)	C (7)	C (1)	117.2 (5)
C (2)	C (1)	C (7)	122.7 (5)	O (1)	C (7)	C (9)	120.6 (4)
C (6)	C (1)	C (7)	118.7 (5)	C (1)	C (7)	C (9)	122.3 (4)
C (1)	C (2)	C (3)	120.2 (5)	C (7)	C (9)	C (10)	120.4 (4)
C (2)	C (3)	C (4)	120.2 (5)	O (2)	C (10)	C (9)	122.7 (4)
C (3)	C (4)	C (5)	120.2 (5)	O (2)	C (10)	C (10)	114.8 (5)
C (4)	C (5)	C (6)	119.8 (6)	C (9)	C (10)	C (10)	122.5 (6)

The C-C bond lengths of the chain also reflect the existence of the dienol. The C(9)-C(10) bond, with distance 1.355(6) Å, is significantly shorter than the other C-C bonds in the chain. Both keto-enol systems are almost completely planar, as expected for a delocalized α system.

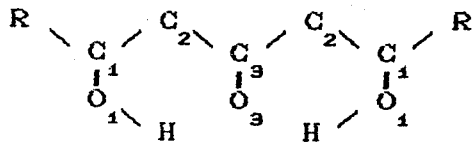
A theoretical study has been described for pentanetrione as a model compound for the study of the molecular geometry of open-chain triketones[10]. This study suggests that the most stable confirmation would be a non-planar one with the two external keto groups oriented opposed to the central one. Nevertheless, in the aryl-substituted triketone[6] and tetraketone reported herein, the existence of the keto-enol system must stabilize the planar conformation.

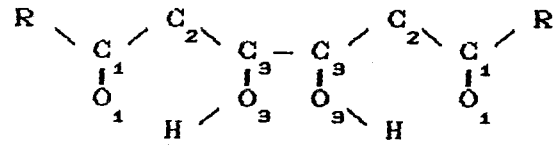
A comparison of the molecular structure of 1,5-diphenylpentane-1,3,5-trione and 1,6-diphenylhexane-1,3,4,6-tetrone shows that there are no significant differences in the ligand parameters and these are illustrated in Table 3.

Table 3
Comparison of bond lengths (Å)

Compound	C_1-R	C_1-C_2	C_2-C_3	C_1-O_1	C_3-O_3
Trion	1.475 (3)	1.361 (3)	1.434 (3)	1.339 (2)	1.288 (2)
Tetrone	1.493 (6)	1.420 (7)	1.355 (6)	1.226 (5)	1.318 (5)

Average values are given for C_1-R, C_1-C_2, C_2-C_3, C_1-O_1 and C_3-O_3.





EXPERIMENTAL

The tetraketone ligand was prepared according to the method of Osadchü and Barkhash11. Crystals were grown by slow evaporation from an acetone solution.

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