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REFINEMENT OF THE STRUCTURE OF THE PRODUCTS OF THE INTERACTION OF 4-OXOALKANE-1,1,2,2-TETRACARBONITRILES WITH ALDEHYDES

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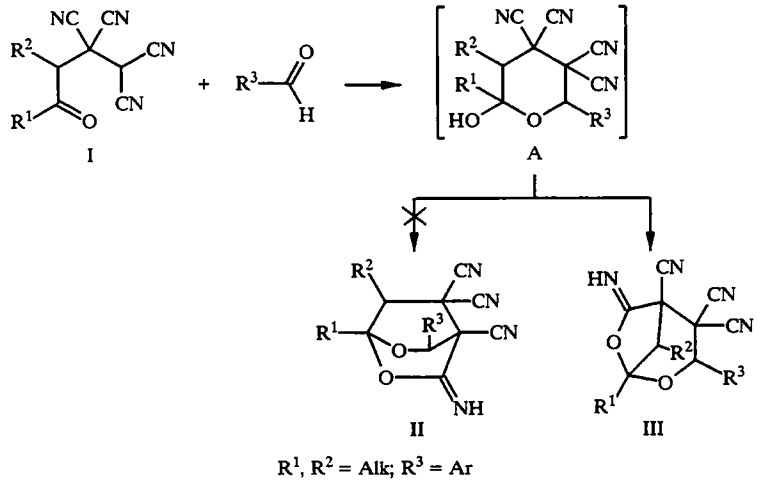
It has been established by x-ray structural analysis that on reacting 4-oxoalkane-1,1,2,2-tetracarbonitriles with aldehydes 6-imino-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitriles are formed and not 3-imino-2,6-dioxabicyclo[2,2,2]octane-4,8,8-tricarbonitriles as had been proposed.

It was reported previously [1] that the reaction of 4-oxoalkane-1,1,2,2-tetracarbonitriles with aldehydes leads to the formation of 3-imino-2,6-dioxabicyclo[2.2.2]octane-4,8,8-tricarbonitriles (II) the structure of which was based on IR, ^{13}C NMR,. and mass spectral data.



R^1, R^2 = Alk; R^3 = Ar

It was shown recently by us [2] that on reacting compound (I) with 1,3,5-triaryl-2,4-diazapenta-1,4-dienes 2-aryl-5,6-dialkyl-6-hydroxypiperidine-3,3,4,4-tetracarbonitriles were formed as intermediate compounds, the structure of which was such that a 1,3-interaction of hydroxyl and a cyano group was preferred. This fact led us to the idea that a similar 1,3 interaction takes place in the reaction of compound (I) with aldehydes to the intermediate (A) as a result of which 6-imino-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitriles (III) are formed and not 3-imino-2,6-dioxabicyclo[2.2.2]octane-4,8,8-tricarbonitrile (II). The correctness of this hypothesis was confirmed by the x-ray structural investigation of a monocrystal of compound (III) [$R^1 + R^2 = (CH_2)_4$, R^3 = Ph] (see Fig. 1).

EXPERIMENTAL

Compound (III) [$R^1 + R^2 = (CH_2)_4$, R^3 = Ph] was obtained by the procedure of [1].

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TABLE 1. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) of 6-Imino-1,8-tetramethylene-3-phenyl-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitrile

Atom	x	y	z	U(eq)
O(1)	4630(2)	6960(1)	2742(1)	32(1)
O(2)	3741(2)	8651(1)	2082(1)	33(1)
N(1)	-1954(3)	8706(2)	2818(1)	53(1)
N(2)	1029(3)	5708(2)	3823(1)	63(1)
N(3)	1873(3)	9495(2)	4280(1)	65(1)
N(4)	2021(3)	10271(2)	2465(1)	40(1)
C(1)	1335(3)	8114(2)	2702(1)	29(1)
C(2)	2274(3)	7776(2)	3400(1)	31(1)
C(3)	4330(3)	7700(2)	3308(1)	30(1)
C(4)	3661(3)	7325(2)	2146(1)	30(1)
C(5)	4518(3)	6732(2)	1570(1)	39(1)
C(6)	3414(4)	6892(3)	917(1)	47(1)
C(7)	1511(3)	6497(3)	992(1)	49(1)
C(8)	647(3)	7221(2)	1532(1)	40(1)
C(9)	1698(3)	7081(2)	2203(1)	31(1)
C(10)	2365(3)	9164(2)	2404(1)	30(1)
C(11)	-523(3)	8437(2)	2765(1)	34(1)
C(12)	1567(3)	6609(2)	3646(1)	38(1)
C(13)	2002(3)	8748(2)	3897(1)	40(1)
C(14)	5409(3)	7233(2)	3906(1)	33(1)
C(15)	6226(3)	8086(2)	4333(1)	43(1)
C(16)	7260(4)	7706(3)	4884(1)	53(1)
C(17)	7510(4)	6483(3)	5004(1)	56(1)
C(18)	6714(4)	5631(3)	4580(1)	53(1)
C(19)	5656(3)	5998(2)	4032(1)	41(1)

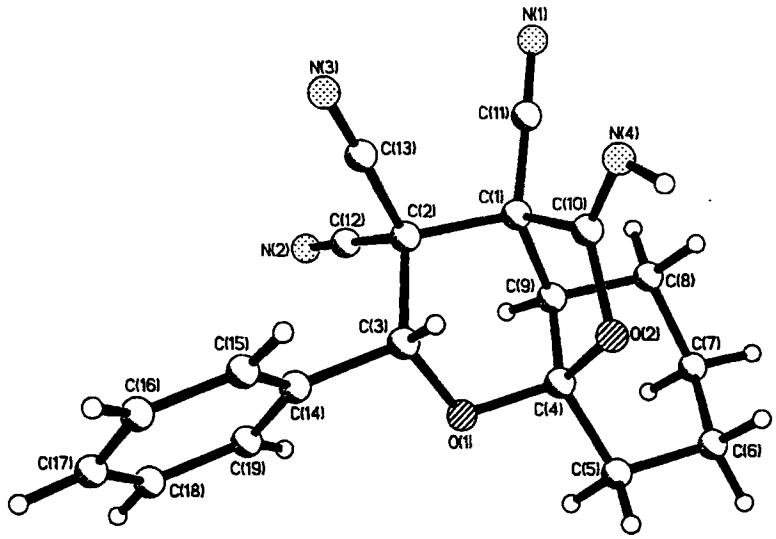

Fig. 1. Structure of 6-imino-1,8-tetramethylene-3-phenyl-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitrile.

X-Ray Structural Investigation of Compound (III) [$R^1 + R^2 = (CH_2)_4$, $R^3 = Ph$]. Crystals were monoclinic, space group $P2_1/c$, at $-80°C$ $a = 7.583(1)$, b = 10.931(3), c = 20.109(4) Å, $\beta = 93.15(2)°$, V = 1664.3(6) $Å^3$, Z = 4, $d_{calc} = 1.324$ g/cm^3. Unit cell parameters and intensities of 3298 reflections were measured on a Syntex $P2_1$ automatic four-circle diffractometer (T = $-80°C$, λMoKα, graphite monochromator, $\theta/2\theta$ scanning, $\theta_{max} = 27°$). Structure was solved by

TABLE 2. Bond Lengths and Valence Angles in 6-Imino-1,8-tetramethylene-3-phenyl-2,7-dioxabicyclo[3.2.1]octane-4,4,5-tricarbonitrile

Bond	Length, Å	Angle	ω, deg	Angle	ω, deg
O(1)—C(3)	1,424(2)	C(21)—O(22)—C(23)	106,0(2)	C(10)—N(1)—C(2)	121,5(2)
O(1)—C(4)	1,428(2)	C(3)—O(1)—C(4)	114,5(2)	C(10)—O(2)—C(4)	109,2(2)
O(2)—C(10)	1,377(3)	C(11)—C(1)—C(10)	111,5(2)	C(11)—C(1)—C(9)	116,0(2)
O(2)—C(4)	1,456(3)	C(10)—C(1)—C(9)	100,4(2)	C(11)—C(1)—C(2)	111,6(2)
N(1)—C(11)	1,135(3)	C(10)—C(1)—C(2)	107,9(2)	C(9)—C(1)—C(2)	108,6(2)
N(2)—C(12)	1,131(3)	C(12)—C(2)—C(13)	109,1(2)	C(12)—C(2)—C(1)	110,1(2)
N(3)—C(13)	1,131(3)	C(13)—C(2)—C(1)	111,0(2)	C(12)—C(2)—C(3)	111,8(2)
N(4)—C(10)	1,245(3)	C(13)—C(2)—C(3)	107,0(2)	C(1)—C(2)—C(3)	107,9(2)
C(1)—C(11)	1,464(3)	O(1)—C(3)—C(14)	110,0(2)	O(1)—C(3)—C(2)	109,0(2)
C(1)—C(10)	1,529(3)	C(14)—C(3)—C(2)	114,9(2)	O(1)—C(4)—O(2)	109,3(2)
C(1)—C(9)	1,545(3)	O(1)—C(4)—C(5)	107,5(2)	O(2)—C(4)—C(5)	109,9(2)
C(1)—C(2)	1,582(3)	O(1)—C(4)—C(9)	110,3(2)	O(2)—C(4)—C(9)	103,1(2)
C(2)—C(12)	1,480(3)	C(5)—C(4)—C(9)	116,6(2)	C(4)—C(5)—C(6)	111,9(2)
C(2)—O(13)	1,480(3)	C(7)—C(6)—C(5)	111,1(2)	C(8)—C(7)—C(6)	111,7(2)
C(2)—C(3)	1,582(3)	C(7)—C(8)—C(9)	110,6(2)	C(4)—C(9)—C(8)	112,2(2)
C(3)—C(14)	1,506(3)	C(4)—C(9)—C(1)	97,5(2)	C(8)—C(9)—C(1)	113,2(2)
C(4)—C(5)	1,505(3)	N(4)—C(10)—O(2)	127,7(2)	N(4)—C(10)—C(1)	125,2(2)
C(4)—C(9)	1,523(3)	O(2) — C(10)—C(1)	107,1(2)	N(1)—C(11)—C(1)	178,8(2)
C(5)—C(6)	1,527(3)	N(2)—C(12)—C(2)	178,7(3)	N(3)—C(13)—C(2)	176,9(3)
C(6)—C(7)	1,522(4)	C(19)—C(14)—C(15)	119,3(2)	C(19)—C(14)—C(3)	122,6(2)
C(7)—C(8)	1,521(4)	C(15)—C(14)—C(3)	118,1(2)	C(16)—C(15)—C(14)	120,5(2)
C(8)—C(9)	1,536(3)	C(17)—C(16)—C(15)	120,0(2)	C(16)—C(17)—C(18)	119,9(2)
C(14)—C(19)	1,385(3)	C(17)—C(18)—C(19)	120,7(3)	C(14)—C(19)—C(18)	119,6(2)
C(14)—C(15)	1,390(3)				
C(15)—C(16)	1,384(4)				
C(16)—C(17)	1,371(4)				
C(17)—C(18)	1,378(4)				
C(18)—C(19)	1,387(4)				

the direct method and refined by full matrix least squares in an anisotropic approach for the nonhydrogen atoms. The hydrogen atoms were located objectively with a Fourier difference synthesis refined in an isotropic approach. The final divergence factors $R_1 = 0.051$ at 3003 independent reflections with $I > \sigma(I)$ and $wR_2 = 0.140$ for each of 3022 independent reflections. All calculations were carried out on an IBM PC/AT 486 with SHELXTL PLUS and SHELXL-93 programs. The coordinates of atoms, bond lengths, and valence angles are given in Tables 1 and 2.

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