

ISSN 0011-1643
UDC 541.571.9
CCA-2001

Original Scientific Paper

Intramolecular Hydrogen Bonds in Quadricyclane Derivatives*

*Hermann Irngartinger** and Rainer Jahn*

*Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270,
D-6900 Heidelberg, Deutschland*

Received May 13, 1991

Two bulky hydroxy-isopropyl substituents on the quadricyclane **2** generate a compression of the intramolecular hydrogen bond (014...015 2.687 Å) and a lengthening of the C1-C5 bond (1.573 Å) of the four membered ring. The corresponding values of the bis(hydroxymethyl) derivative **1** are 010...011 2.799 Å and C1-C5 1.546 Å, respectively.

INTRODUCTION

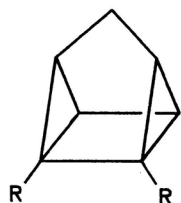
Within a project of determining the bonding system of polycyclic small-membered rings and the influences of substituents on the molecular dimensions of these compounds¹, we established the structure of two quadricyclane derivatives 1,5-bis(hydroxymethyl)quadricyclane (tetracyclo[3.2.0.0.2⁷.0^{4,6}]heptane-1,5-dimethanol) **1** and 1,5-bis(hydroxy-iso-propyl)quadricyclane ($\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dimethanol) **2**. Simultaneous intra- and intermolecular hydrogen bonds are predetermined for these double functional compounds. L. Pauling has worked at hydrogen bond systems extensively.²

RESULTS AND DISCUSSION

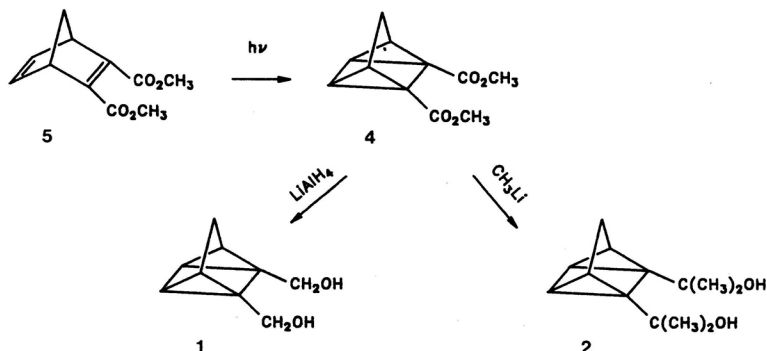
In order to determine the influence of the electron accepting cyano groups on the strained bonds of the quadricyclane system, we investigated the structure of the dicyano derivative **3**.³ For the purpose of comparison we required derivatives with substituents not exerting electronic effects onto the polycyclic systems. Therefore, we synthesized the 1,5-bis(hydroxymethyl)quadricyclane **1** by reduction with LiAlH₄ from the corresponding dimethyl dicarboxylate **4**.⁴ The 1,5-bis(hydroxy-isopropyl)quadricyclane **2** was obtained by treatment of **4** with methyllithium.⁵ The quadricyclane-dicarboxy-

* Dedicated to Professor Linus Pauling on the occasion of this 90th birthday.

** Author to whom correspondence should be addressed.

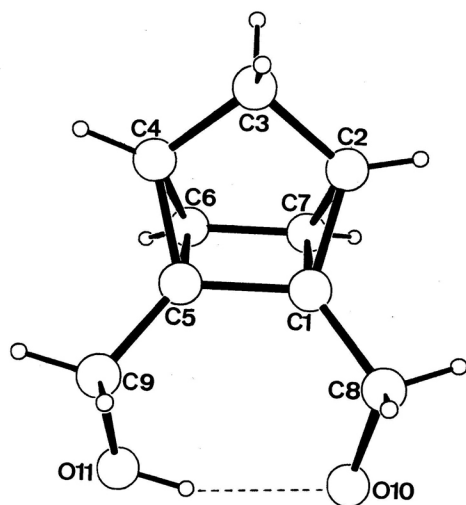


- 1: R=CH₂OH
 2: R=C(CH₃)₂OH
 3: R=CN
 4: R=CO₂CH₃

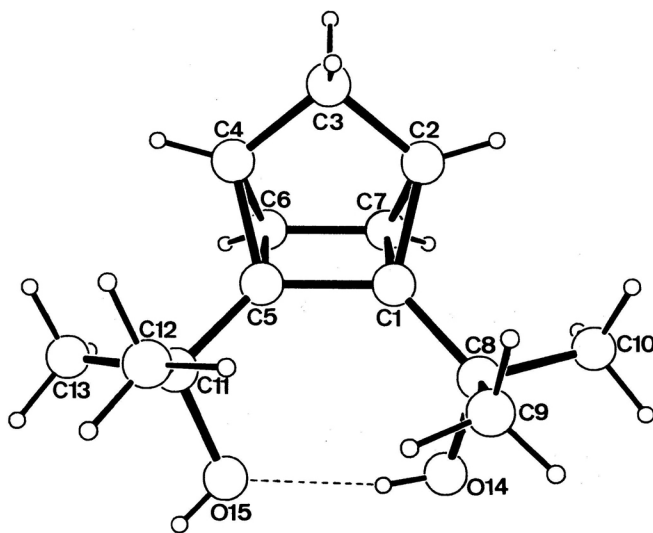


late **4**⁶ is available from the dimethyl bicyclo[2.2.1]hept-2,5-diene-2,3-dicarboxylate **5** by photochemical, intramolecular [2+2]cycloaddition.⁷

Electron accepting substituents exert significant electronic effects on the bond lengths of quadricyclane.^{3,8} The derivatives **1** and **2** are not influenced by these effects. Therefore, all the bond lengths of the three membered rings have the same order of magnitude (on the average: 1.517(3) Å for **1** and 1.510(8) Å for **2**; Table I) and compare well within the margin of significance with the corresponding values of the 3-oxybenzotrile-quadricyclane **6**, substituted only on the bridging carbon C3 (1.491 Å)⁸ and of quadricyclane (clathrate 1.53 Å⁹; ED 1.51 Å¹⁰, *ab initio* calculation 6-31G 1.519 Å¹¹). However, the C1-C5 bonds on the substituted side of the four membered rings of **1** and **2** are lengthened by repulsive forces between the substituents. The C1-C5 bond (1.573 Å) in **2** compared with C6-C7 (1.518 Å) on the unsubstituted side is considerably more extended than the corresponding bond in **1** (C1-C5 1.546 Å; C6-C7 1.531 Å). The bulky isopropyl groups generate a stronger steric strain in **2** relative to **1**. Both oxygen atoms O14...O15 in the intramolecular hydrogen bond of **2** are compressed to a distance of 2.687 Å, which is shorter than the corresponding distance O15...O14' 2.764 Å of the intermolecular hydrogen bond (Table II). The distances of the corresponding hydrogen bonds in **1** have the opposite sequence: intramolecular O10...O11 2.799(2) Å; intermolecular O11...O10'(2-x, -0.5+y, 1-z) 2.706(2) Å (Table II). The corresponding bond lengths of the unsubstituted fourmembered rings of **6** (1.544 Å)⁸ and of quadricyclane (clathrate 1.53 Å⁹; ED 1.565 Å¹⁰, *ab initio* calculation 6-31G 1.549 Å¹¹) are shorter than the highly strained C1-C5 bond of **2**.



1



2

Figure 1. Molecular Structure of 1 and 2.

TABLE I
Bond lengths (Å) of 1 and 2

1		2	
C1-C2	1.518(2)	C1-C2	1.512(3)
C1-C5	1.546(2)	C1-C5	1.573(3)
C1-C7	1.517(2)	C1-C7	1.509(3)
C1-C8	1.488(2)	C1-C8	1.516(3)
C2-C3	1.506(2)	C2-C3	1.495(3)
C2-C7	1.517(3)	C2-C7	1.499(3)
C3-C4	1.511(3)	C3-C4	1.492(3)
C4-C5	1.520(2)	C4-C5	1.519(3)
C4-C6	1.516(3)	C4-C6	1.504(3)
C5-C6	1.512(3)	C5-C6	1.517(3)
C5-C9	1.485(3)	C5-C11	1.501(3)
C6-C7	1.531(3)	C6-C7	1.518(3)
C8-O10	1.434(2)	C8-C9	1.512(3)
C9-O10	1.434(2)	C8-C10	1.517(3)
		C8-O14	1.441(2)
		C11-C12	1.515(3)
		C11-C13	1.523(3)
		C11-O15	1.441(3)

TABLE II
Hydrogen bond systems in 1 and 2

1		2	
intramolecular			
011...010	2.799(2)	014...015	2.687(3)
011-H11...010	162(3) ^a	014-H14...015	167(3) ^a
intermolecular			
011...010'	2.706(2)	015...014'	2.764(2)
(2-x, -0.5+y, 1-z)		(0.5-x, 0.5+y, 1.5-z)	

EXPERIMENTAL

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dimethanol **1**, 1,5-bis(hydroxymethyl)quadricyclane **1** was obtained in an oily mixture with other compounds.⁴ We synthesized and isolated pure crystals according to the following procedure.

A solution of 1 gr (0.0048 mol) quadricyclane-dicarboxylate **4**¹² in 10 ml absolute ether was slowly added to 0.364 g (0.0096 mol) lithium aluminiumhydride elutriated in 15 ml absolute ether and refluxed for 1 hour. The excess of LiAlH₄ was destroyed by adding a saturated Na₂SO₄ solution. The salt residue was sucked off and washed with ether. The ether was removed and the residual yellow oil was recrystallized several times at -30 °C from acetone. Yield 0.52 g (0.0034 mol; 71% colourless prisms, m.p. 73 °C).

¹H-NMR (300 MHz, CDCl₃, 294 K): δ = 3.94, 3.61 (AM, d 2H, d 2H, J_{AM} = 12.5 Hz, -CH₂-O), 3.86 (br s, 2H, -OH), 2.01, 1.92 (AM, d 1H, d 1H, J_{AM} = 11.1 Hz, -CH₂-), 1.80, 1.46 (AX, d 2H, d 2H, J_{AX} = 4.4 Hz, -CH). IR (KBr): 3270 br (-OH), 2920 s, 2850 s (C-H), 1450 s, 1005 s, 875 m [cm⁻¹].

MS(high resolution): M⁺ (C₉H₁₂O₂) calc 152.0837, obs 152.0833, 032% m/e: 134 (M-H₂O)12.48%; 121 (M-CH₂OH) 25.98%; 105 (C₈H₉) 44.32%; 103 (M-CH₂OH, -H₂O) 28.64%; 91

TABLE IV

Atomic coordinates and the equivalent atomic displacement parameters ($X10^3\text{\AA}^2$) of **1** and **2**.
 U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor

	Atom	x	y	z	$U_{eq} \times 10^3$
1	C1	0.6749(3)	0.3429	0.2890(2)	28(1)
	C2	0.6195(3)	0.4853(3)	0.1758(2)	36(1)
	C3	0.6291(3)	0.4050(3)	0.0270(2)	37(1)
	C4	0.8189(3)	0.2653(3)	0.0528(2)	37(1)
	C5	0.8090(3)	0.1950(2)	0.2064(2)	29(1)
	C6	0.9933(3)	0.3324(4)	0.1663(2)	42(1)
	C7	0.8613(3)	0.4792(3)	0.2480(2)	40(1)
	C8	0.5516(3)	0.3190(3)	0.4278(2)	34(1)
	C9	0.8376(3)	0.0043(3)	0.2521(2)	36(1)
	O10	0.7023(2)	0.2452(2)	0.5385(1)	36(1)
	O11	0.9627(3)	-0.0106(3)	0.3873(2)	48(1)
2	C 1	0.3763(1)	0.1923(2)	0.6078(2)	41(1)
	C 2	0.4272(1)	0.1320(3)	0.5349(2)	60(1)
	C 3	0.4666(1)	0.2486(3)	0.4848(2)	62(1)
	C 4	0.4133(1)	0.3614(3)	0.4786(2)	51(1)
	C 5	0.3668(1)	0.3520(2)	0.5694(1)	40(1)
	C 6	0.3451(1)	0.2943(3)	0.4640(2)	56(1)
	C 7	0.3548(1)	0.1404(3)	0.5014(2)	60(1)
	C 8	0.3581(1)	0.1245(2)	0.7101(2)	46(1)
	C 9	0.3994(1)	0.1832(3)	0.8005(2)	73(2)
	C10	0.3638(1)	-0.0385(3)	0.7053(2)	78(2)
	C11	0.3435(1)	0.4840(2)	0.6253(2)	49(1)
	C12	0.3997(1)	0.5491(3)	0.6912(2)	72(2)
	C13	0.3150(1)	0.5961(3)	0.5501(2)	74(2)
	O14	0.2883(1)	0.1514(2)	0.7283(1)	56(1)
	O15	0.2905(1)	0.4362(2)	0.6907(1)	68(1)

TABLE III

Crystallographic data and refinement parameters of **1** and **2**

	1	2
Formula	C ₉ H ₁₂ O ₂	C ₁₃ H ₂₀ O ₂
Molec. mass	152.19	208.3
Crystal size [mm]	0.6x0.55x0.25	0.4x0.4x0.2
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	C2/c
a [Å]	5.680(2)	19.953(2)
b [Å]	7.415(1)	9.277(1)
c [Å]	9.279(2)	12.924(1)
β [°]	91.07(2)	91.53(1)
V [Å ³]	390.7(3)	2391.4(2)
Temperature [K]	233	293
D_{calc} [Mg·m ⁻³]	1.29	1.16
Z	2	8
F(000)	164	912
($\sin\theta/\lambda$) _{max} [Å ⁻¹]	0.66	0.63
Abs. coeff. μ [mm ⁻¹]	0.084	0.071
Refl. unique	1024	2875
Refl. obs.	974	1320
[I > k. σ (I)];k	3	2
Variables	147	216
R	0.042	0.044
wR	0.054	0.045
max. $\Delta\rho$ [e.Å ⁻³]	0.25	0.25

(C₇H₇) 78.12%, 78 (C₆H₆) 30.84%; 77 (C₆H₅) 60.66%; 66 (C₅H₆) 100%; 39 (C₃H₃) 25.49%; 31 (CH₂OH) 11.65%

Analysis:	calc	obs
C:	71.027%	70.53%
H:	7.95%	8.07%

$\alpha, \alpha', \alpha', \alpha'$ -tetramethyl-tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1,5-dimethanol **2**.

To a solvent of 2 g (0.0096 mol) of **4** 0.04 mol methyl lithium freshly prepared was added. After 2 hours, the lithium salt was hydrolyzed by 20 ml H₂O. The aqueous mixture was extracted with ether and the ether was removed. Yield 1.64 g (0.0078 mol; 82%) of crude **2**. Several times recrystallized from acetone: 1.44 g (0.0069 mol; 72%) colourless crystals m.p. 152 °C (lit.⁵ m.p. 153–155 °C).

Crystallographic Data.

The X-ray structure investigations have been carried out with an Enraf-Nonius CAD 4 diffractometer with Mo-K α radiation, graphite monochromator, ω -2 θ scanning. The structures have been solved by direct methods (SDP program system¹³). The X-ray data of **1** were collected at -40 °C because of its instability. The crystallographic data and the refinement parameters are listed in Table III, the atomic coordinates of **1** and **2** and the averaged anisotropic thermal parameters (U_{eq}) are given in Table IV.¹⁴

REFERENCES

1. P. Dowd and H. Irngartinger, *Chem. Rev.* **89** (1989) 985.
2. L. Pauling, *Die Natur der chemischen Bindung*, Verlag Chemie, Weinheim, third edition, 1976, p. 422-469.
3. H. Irngartinger, R. Jahn, H. Rodewald, C. T. Kiers, and H. Schenk, *Acta Cryst. C* **42** (1986) 847.
4. U. Heywang and G. Szeimies, *Chem. Ber.* **123** (1990) 121.
5. R. Criegee, R. Askani and H. Grüner, *Chem. Ber.* **100** (1967) 3916.
6. S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.* **76** (1954) 5000.
7. G. Kaupp and H. Prinzbach, *Helv. Chim. Acta* **52** (1969) 956.
8. W. H. Watson, I. Tavanaiepour, A. P. Marchand, and P. R. Dave, *Acta Cryst. C* **43** (1987) 1356.
9. V. M. Coiro, E. Giglio, F. Mazza, N. V. Pavel, *J. Inclusion Phenomena* **1** (1984) 329.
10. K. Mizuno, T. Fukuyama, and K. Kuchitsu, *Chem. Lett.* (1972) 249.
11. K. Raghavachari, R. C. Haddon, and H. D. Roth, *J. Amer. Chem. Soc.* **105** (1983) 3110.
12. T. C. Morrill, S. Malasanta, K. M. Warren, and B. E. Greenwald, *J. Org. Chem.* **40** (1975) 3032.
13. B. A. Frenz, Ass. Inc. College Station, Texas, USA, and Enraf-Nonius, Delft, Holland (1982).
14. Further details concerning the X-ray investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55276, the names of the authors and the journal citation.

SAŽETAK

Intramolekularna vodikova veza kod novih derivata kvadriciklena

H. Irngartinger i R. Jahn

Geometrijska struktura kvadriciklena supstituiranog velikim hidroksi-izopropilnim skupinama na položajima C₁ i C₅ određena je metodom difrakcije X-zraka. Strukturni parametri uspoređeni su s podacima za bis-hidroksimetil-derivat kvadriciklena. Utvrđeno je da se udaljenost između atoma kisika smanjuje, dok se duljina veze C₁-C₅ povećava.