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N,N'-Linked 1,2-Ethanediyl-Poly(Benzimidazolin-2-ones) and the X-Ray Crystal Structure of a Benzimidazolin-2-one Trimer

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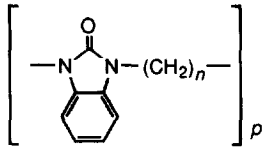
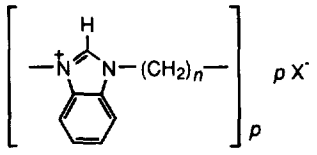
Abstract.— A series of N,N'-linked 1,2-ethanediyl-poly(benzimidazolin-2-ones) that can be classified as podands, are described. Seven dimers (**21-27**), three trimers (**28-30**), a cyclic tetramer (**31**) and an open-chain benzimidazolin-2-one heptamer (**32**) have been prepared and characterized by ^{1}H, ^{13}C NMR and by MS. The crystal and molecular structure of the trimer, 1,3-bis-2-(2-oxobenzimidazol-1-yl)ethyl-2-oxobenzimidazole monohydrate (**30**) has been solved by X-Ray analysis. The benzi-midazolin-2-one fragments display a pattern of bond distances and angles similar to that of analogue derivatives retrieved form the CSD. The molecules are hydrogen bonded to four others in a continuous two-dimensional network by N-H···O=C and C-H···O=C interactions in which all N-H donors and O=C acceptors are involved. © 1997 Elsevier Science Ltd.

INTRODUCTION

In order to correctly situate this paper's contribution to the topic, let us briefly summarize the knowledge about neutral *N,N'*-poly(benzimidazolin-2-ones) (benzimidazolin-2-ones are often improperly called benzimidazolones) **1** and the related *N,N'*-polybenzimidazolium salts **2** both linear and cyclic will allow to better situate our own contribution.

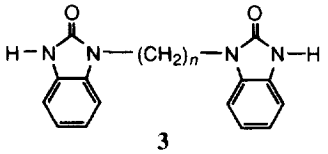


1



2

Pozharski described the reaction of bis(1-benzimidazolyl)alkanes with potassium hydroxide which affords bis(1-benzimidazolin-2-ones) **3** when n = 3-5 (for n = 1 or 2 the alkanes decompose).[1] Compound **3**, n = 3 [1,1'-(1,3-propandiyl)bis(benzimidazolin-2-one] was also prepared by Weber by treating 1-isopropenyl-benzimidazolin-2-one with 1,3-dibromopropane.[2] More recently, Thummel prepared compounds **4** (n = 4) by deprotonation and oxidation by air of the corresponding benzimidazolium salt (see later on).[3]



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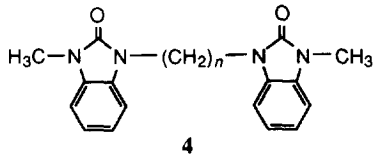
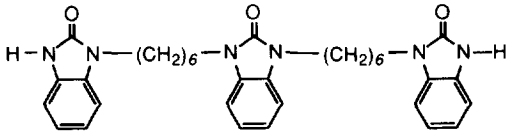


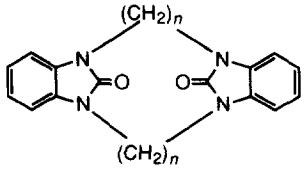
4

The main contribution to polybenzimidazolinone chemistry was due to Meth-Cohn.[4-8] This author prepared derivatives of compounds **3** and **4** with n = 3, 4, 5, 6, 7, 10, 12 and 20. He also prepared an open-chain trimer **5**.[8]



5

The first macrocycles formed by benzimidazolin-2-one units **1** were prepared by Meth-Cohn, for instance **6** (n = 5, 6, 7, 8 and 10) and **7** (n = 4 and 6).[6] Afterwards, Weber prepared the trimer **8** (**7**, n = 3) and determined its complexation constants towards several cations.[2]



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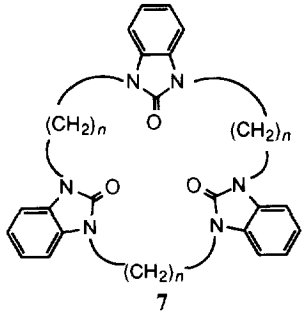

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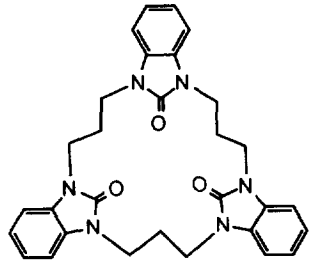
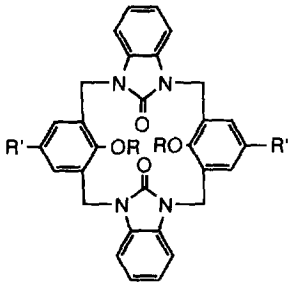
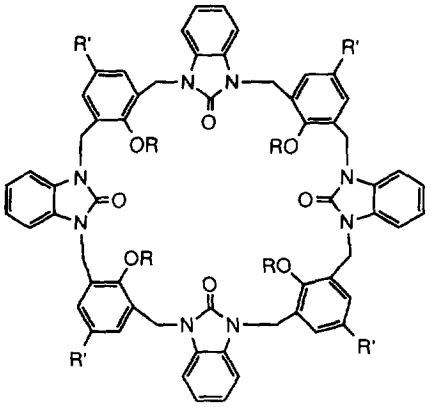


8

Thummel has also prepared the ureaphanes **6** (n = 3, 4) by oxidation of the corresponding 2,2'-dibenzimidazolidinylidene (see later on)[9] as well as the tetramer (n = 3) corresponding to **8** by deprotonation /oxidation of the corresponding benzimidazolium salts (see later on).[3] Very recently, Weber reported the synthesis and X-ray structural studies of solvent inclusions of a series of heterocalixarenes featuring the benzimidazolin-2-one subunit **9a** and **9b**.[10]

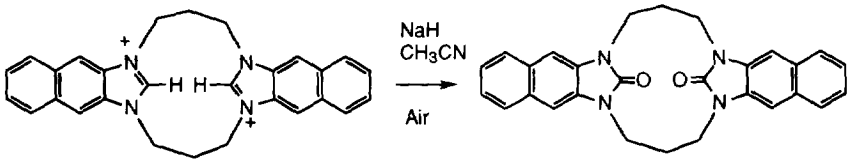


9a



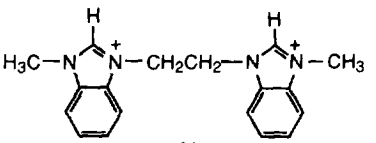
9b

Concerning *N,N'*-disubstituted polybenzimidazolium salts **2** and the corresponding benzimidazolinylidenes we have already reported that Thummel[3,9] used these compounds as precursors of compounds **4** and **6**. Recently, he described a related pair of derivatives (**10** and **11**).[11]



10 **11**

In summary, the results so far obtained correspond: i) to polymethylene chains $n \geq 3$; ii) to p = 2-4 benzimidazolinone units; iii) to p = 2 (open) or p = 4 (ring) benzimidazolium units. The purpose of this paper is to explore the case n = 2 (ethanediyl). This case is the most complex [the simpler case of n = 1, methanediyl, has been reported for bis(benzimidazolium) derivatives][12] since both benzimidazolinones and especially benzimidazolium salts are good leaving groups which make the formation of *N*-vinyl compounds a competitive reaction.[13] To the best of our knowledge, so far the only known compound is the double quaternary salt **12**.[14]



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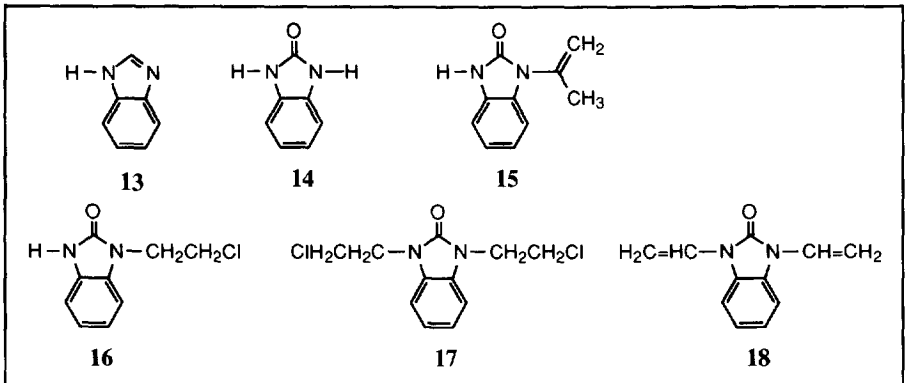
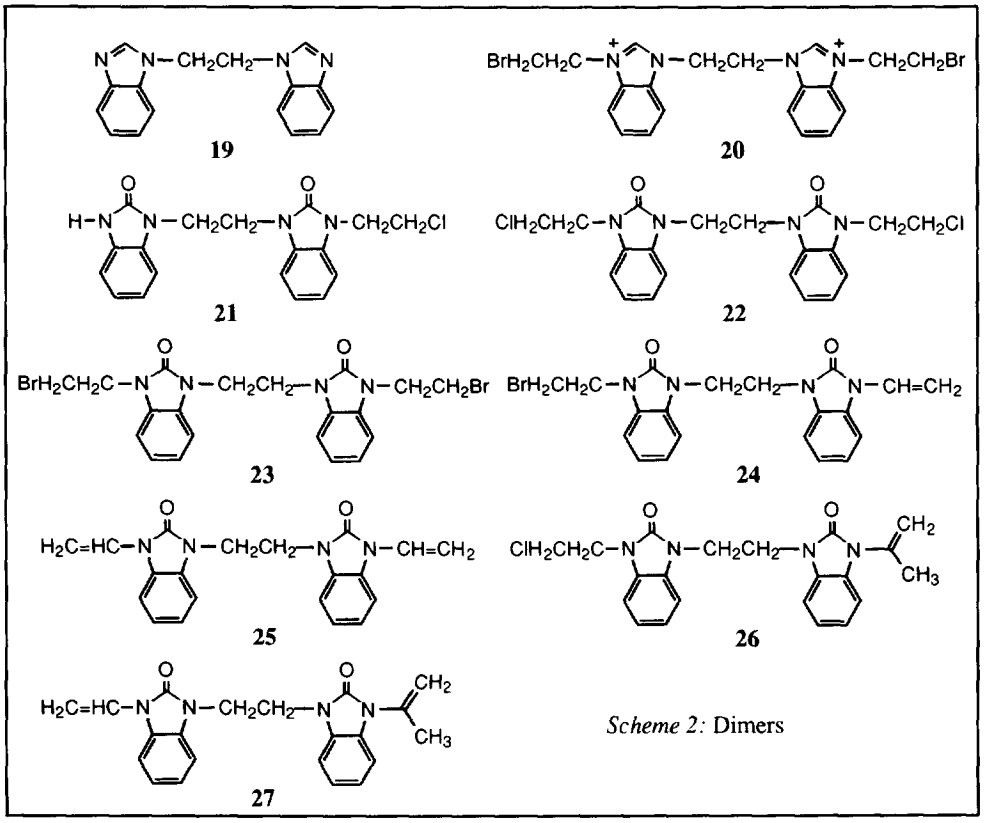
RESULTS AND DISCUSSION

Chemistry

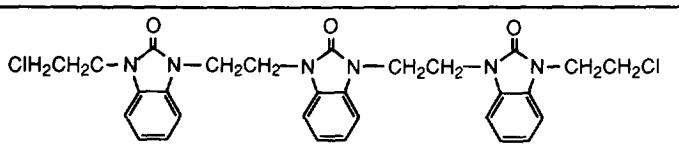
Due to the complexity of the reactions, we have preferred to summarize in Schemes 1 to 5 the different molecules involved in this work.



Scheme 1: Monomers



Scheme 2: Dimers



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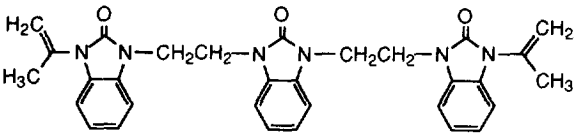

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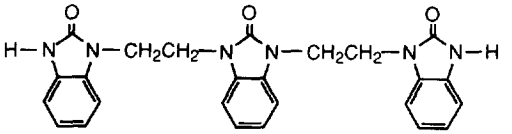
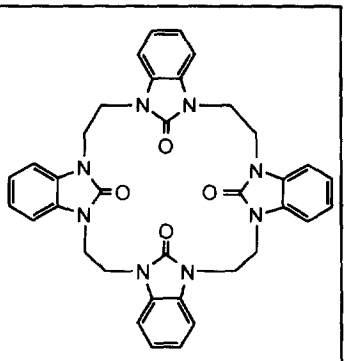


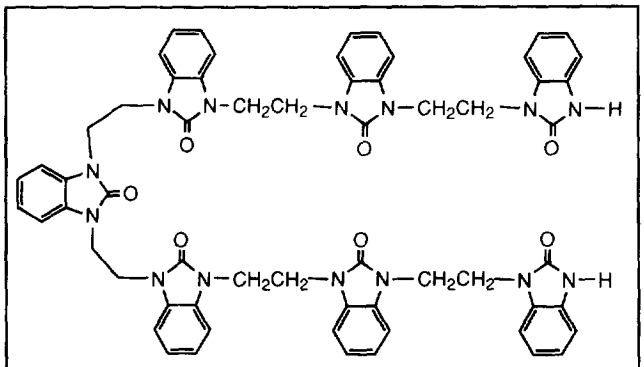
30

Scheme 3: Trimers



31

Scheme 4: Tetramer



32

Scheme 5: Heptamer

Benzimidazoles and benzimidazolium salts. Starting from benzimidazole **13** the reaction with 1,2-dibromoethane in different PTC conditions led to bis(benzimidazol-1-yl)ethane **19**, a compound already described.[13] The treatment of **19** with 2 equivalents of 1,2-dibromoethane yields the double quaternary salt **20**; no macrocyclic structures were detected. This rather unstable compound, is oxidized by air in basic medium, depending on the base, to **23** and **24** (Et_3N) or to **25** (NaH like Thummel).[11] The strongest base produces the total elimination of HBr.

Benzimidazolin-2-ones. The reaction of benzimidazolinone **14** with 1,2-dichloroethane in PTC affords different products depending on the small experimental differences (see experimental part). Monomers **16** and **17**, dimers **21** and **22**, and the trimer **28** were isolated and fully characterized while tetramer **31** was formed in very low amount and its structure was established by mass spectrometry (see below). However, the construction

of *N,N'*-linked 1,2-ethanediyl-poly(benzimidazolin-2-ones) can be achieved by a synthetic scheme of protection of compound **14**, alkylation with 1,2-dichloroethane, and deprotection. As protecting group we have used the 2-propenyl group since it has been employed with success in benzimidazole chemistry.[2,15-17]

1-Isopropenylbenzimidazolin-2-one **15** and 1,3-di(2-chloroethyl)-benzimidazolin-2-one **17** obtained previously, were allowed to react in different conditions: i) in PTC conditions (toluene, KOH, tetrabutylammonium bromide [TBAB]) the reaction affords a mixture of **26**, **27** and **29** all of them in very low yields (the most abundant, **29**, was formed in 8.5% yield). ii) in another PTC conditions (acetonitrile, K_2CO_3, tetrabutylammonium bisulfate) a mixture of **18**, **27** and **29** was obtained, but the yield of **29** was 78%. iii) in a microwave oven in the presence of KOH the same mixture was obtained but the yield of trimer **29** was only 49%. Since this was the desired product, conditions ii) were selected to prepare a larger quantity of the trimer which was subsequently deprotected cleaving off the two isopropenyl groups by treatment with HCl in hydro-alcoholic solution: trimer **30** was obtained in 89% yield.

The reaction between trimer **30** and 1,3-di(2-chloroethyl)-benzimidazolin-2-one **17** was expected to offer a way of preparing tetramer **31** but, although a 1:1 molar ratio and high dilution techniques were used, the only compound isolated in reasonable yield was heptamer **32**.

^{1}H and ^{13}C NMR spectroscopy

Assignment of the NMR resonances of dimers **21-27**, trimers **28-30** and heptamer **32** was done by comparison with the monomer **15** and the symmetrically substituted compounds **17**, **18** and **19**, because in these compounds only one chain NCH_2CH_2N, NCH_2CH_2Cl, $NCH{=}CH_2$ or $NC(CH_3)CH_2$ is present. Cyclic tetramer **31** was isolated in too small amount to be characterized by NMR.

In ^{1}H-NMR, the NCH_2CH_2N groups appear as broad singlets even if they are substituted by two different benzimidazolin-2-one derivatives. The $NCH_2CH_2Cl(Br)$ group shows two triplets, being the NCH_2 group the less shielded. The $NCH{=}CH_2$ group was assigned considering the coupling constants in the vinyl group.[13] Finally, the geminal protons of the $NC(CH_3)CH_2$ group were assigned by NOE difference spectroscopy and considering that in these compounds $^4J_{cis}$ is larger than $^4J_{trans}$. In most cases, signals derived from the aromatic protons are not differentiated.

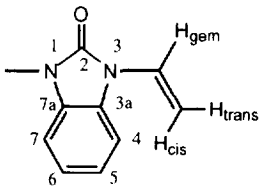


Table 1. ^{1}H NMR of benzimidazolinones (chemical shifts in ppm, coupling constants in Hz)

Comp	Solv[a]	H_4-H_7	CH_2N	$CH_2Cl(Br)$	CH_2[d]	H_{cis}	H_{trans}	H_{gem}	CH_3
14[e]	b	6.90 (bs)	-----	-----	-----	-----	-----	-----	-----
15[e]	b	7.06-7.17	-----	-----	-----	5.41(q)	5.25(q) J = 1.2, J = 0.6	-----	2.25(dd)
16[e]	c	7.09-6.85	4.11(t) J = 6.6	3.68(t)	-----	-----	-----	-----	-----

17	c	7.08-7.15	4.22(t) 3.82(t) J = 6.7	-----	-----	-----	-----	-----	
18	c	7.18-7.35	----- ------	-----	5.67(dd) 5.50(dd) 7.01(dd) J_{ct} = 1.0, J_{tg} = 9.5, J_{cg} =16.1			-----	
21[e]	c	6.80-7.20	4.10(t) 3.67(t) J = 6.4	4.25(s)	-----	-----	-----	-----	
22	c	6.83-7.04	4.10(t) 3.67(t) J = 6.5	4.24(s)	-----	-----	-----	-----	
23	c	6.82-7.02	4.19(t) 3.52(t) J = 6.8	4.24(s)	-----	-----	-----	-----	
24	c	6.82-7.19	4.17(t) 3.49(t) J = 6.8	4.24(s) J_{ct} = 1.0, J_{tg} = 9.3, J_{cg} =16.4	5.55(dd)	5.00(dd)	(under H_4-H_7)		
25	c	6.97-7.21	----- -----	4.24(s) J_{ct} = 1.0, J_{tg} = 9.5, J_{cg} =16.1	5.55(dd)	5.00(dd)	6.97(dd)		
26	c	6.83-6.96	4.10(t) 3.68(t) J = 6.6	4.22(s)	5.28(q) J = 1.2	5.04(s)	-----	2.10 J = 1.2	
27	c	6.86-7.20	----- -----	4.23(s)[f] J_{ct} = 1.0, J_{tg} = 9.3, J_{cg} =16.4	5.55(dd)[f]	4.95(dd)[f]	(under H_4-H_7)		
					5.29(q)[g]	5.06(q)[g] J = 1.4, J = 0.8	-----	2.13(dd)	
28	c	6.70-7.15	3.30-3.40	-----	-----	-----	-----	-----	
29	c	6.78-6.98	4.20 -----	-----	5.27	5.05	-----	2.10	
30[e]	b	6.75-6.92	3.89-3.99 -----	10.8	-----	-----	-----	-----	
32[e]	c	6.83-7.00	3.98-4.14 -----	10.6	-----	-----	-----	-----	

[a]: b = DMSO-d_6, c = $CDCl_3$; [d] central CH_2CH_2 in dimers, trimers and heptamer; [e] δNH ≈ 10.4-10.8 ppm (broad); [f] vinyl: [g] isopropenyl.

In the ^{13}C-NMR spectra, signals from the aromatic carbons are different even if the heterocyclic rings are very similar. They have been assigned by comparison with the symmetrically substituted monomers and dimers but some of them can be interchanged. Compound **28** decomposes in solution and its ^{13}C NMR spectrum cannot be properly recorded. Compounds **16** and **21** were obtained in too low quantities for ^{13}C NMR spectroscopy.

Table 2. ^{13}C NMR of benzimidazolinones (chemical shifts in ppm)

Comp	Solv[a]	C2	C3a, C7a	C4, C7	C5, C6	C2'	C3a', C7a'	C4', C7'	C5', C6'
14	b	155.3	129.7, 129.7	108.5, 108.5	120.4, 120.4	-----		-----	----- -----
15	c	154.5	128.3, 130.0	109.1, 109.8	121.3, 121.9	-----		-----	----- -----
16	c	153.8	129.0, 129.1	107.1, 107.7	121.4, 121.5	-----		-----	----- -----
17	c	153.7	129.3, 129.3	108.0, 108.0	121.7, 121.7	-----		-----	----- -----
18	c	152.7	127.7, 127.7	109.6, 109.6	122.6, 122.6	-----		-----	----- -----
22	c	153.7	128.9, 129.0	107.0, 107.7	121.4, 121.5	-----	-----	-----	-----

23	c	153.7	128.8, 129.1	107.1, 107.7	121.4, 121.6	-----	-----		-----		-----
24	c	153.7	128.8, 129.1	107.1, 107.1	121.5, 121.7	-----	-----		107.3, 109.5		121.7, 122.3
25	c	152.8	127.3, 129.1	107.4, 109.5	121.8, 122.4	-----	-----		-----		-----
26	c	152.5	128.9, 129.1	107.1, 107.6	121.3, 121.5	-----	128.6,	129.2	106.9, 108.8		121.3, 121.5
27	c	152.7	128.6, 129.2	107.0, 108.9	121.3, 121.7	-----	127.2,	129.2	107.3, 109.4		121.6, 122.3
29	c	153.9	128.8, 128.8	107.1, 107.1	121.5, 121.5	152.5	127.2,	128.6	107.0, 107.3		121.3, 121.6
30	b	153.5	128.9, 128.9	106.9, 106.9	120.9, 120.9	154.1	128.3,	130.1	107.2, 108.7		120.4, 121.0
32	c	154.0	129.1, 129.1	107.2, 107.2	121.5, 121.5	155.8	127.9,	130.4	107.2, 109.4		121.5, 121.5

Comp	Solv[a]	CH_2CH_2	CH_2N	$CH_2Cl(Br)$	$=CH_2$	=CH	CH_3	$=CH_2$	=C
15	c	-----	-----	-----	-----	-----	20.2	113.8	137.8
16	c	-----	42.8	41.1	-----	-----	-----	-----	-----
17	c	-----	43.0	41.2	-----	-----	-----	-----	-----
18	c	-----	-----	-----	102.4	126.7	-----	-----	-----
22	c	39.0	42.8	41.0	-----	-----	-----	-----	-----
23	c	39.1	42.7	28.0	-----	-----	-----	-----	-----
24	c	38.9, 39.0	42.7	29.7	101.5	127.0	-----	-----	-----
25	c	38.8	-----	-----	101.5	127.0	-----	-----	-----
26	c	38.8, 38.9	42.8	41.0	-----	-----	20.0	113.2	137.7
27	c	38.7, 38.8	42.8	41.0	-----	-----	20.0	113.2	137.7
29	c	38.7, 38.8	-----	-----	-----	-----	20.0	113.2	137.4
30	b	38.1, 38.3	-----	-----	-----	-----	-----	-----	-----
32	c	38.8	-----	-----	-----	-----	-----	-----	-----

[a]: b = DMSO-d_6, c = $CDCl_3$

Mass spectrometry

FAB MS has been used to characterize several of the above structures, especially, the cyclic nature of tetramer **31** was only established by MS. Instead of discussing one by one the different compounds we have preferred to summarize the information in Table 3 adding, when necessary, some comments (G = glycerol, NBA = *m*-nitrobenzylic alcohol).

Table 3. Mass spectra of some representative compounds

Comp.	Mol. formula	MW (Da)[a]	Matrix	MH^+	Other fragments
20	$[C_{20}H_{22}N_4Br_2]^{++}$	476	G	475-477-479 (1:2:1)	555-557-559-561 (1:3:3:1) $[CBr]^+$
23	$C_{20}H_{20}N_4O_2Br_2$	506	G, NBA	507-509-511 (1:2:1)	
24	$C_{20}H_{19}N_4O_2Br$	426	G, NBA	427-429 (1:1)	
25	$C_{20}H_{18}N_4O_2$	346	G, NBA	347	186 [**18**], 187
31	$C_{36}H_{32}N_8O_4$	640	NBA	641	481 (M-160)
32	$C_{61}H_{54}N_{14}O_7$	1094	NBA	1095 (100), 1096 (75)	1117 $[MNa]^+$, 1133 $[MK]^+$

[a]For ^{79}Br.

X-ray crystallographic study of trimer 30.

The most relevant intra and intermolecular parameters are given in Table 4 according to the numbering system displayed in Fig. 1a.[18] There are no significant differences between the three benzimidazolinone moieties as tested by half normal probability plots [19] except for the internal angle at the nitrogen atoms. Replacement of one hydrogen atom of five-membered rings with the ethylene chains results in a narrowing of the endocyclic angles at that N atom. A search of the Cambridge Structural Database (CSD hereinafter)[20] revealed only four structures

Table 4. Selected geometrical parameters (Å,°). C(**A**), C(**B**), C(**C**) stand for the centroids of the centroid of the C(4)...C(9), C(28)...C(33) and N(25)..C(33) rings.

a) Benzoimidazolinone moiety			Present work			CSD
N(1)-C(2)	1.379(3)	N(13)-C(14)	1.379(3)	N(25)-C(26)	1.390(3)	1.393(21)
C(9)-N(1)	1.392(3)	C(21)-N(13)	1.392(3)	C(33)-N(25)	1.389(4)	1.402(14)
C(2)-N(3)	1.366(4)	C(14)-N(15)	1.363(4)	C(26)-N(27)	1.359(3)	1.362(10)
N(3)-C(4)	1.400(3)	N(15)-C(16)	1.384(3)	N(27)-C(28)	1.391(4)	1.383(17)
C(4)-C(9)	1.392(4)	C(16)-C(21)	1.397(3)	C(28)-C(33)	1.397(3)	1.396(8)
C(2)-O(10)	1.232(3)	C(14)-O(22)	1.223(4)	C(26)-O(34)	1.226(4)	1.227(13)
C(9)-N(1)-C(2)	109.3(2)	C(21)-N(13)-C(14)	109.6(2)	C(33)-N(25)-C(26)	109.4(2)	109.9(7)
N(1)-C(2)-N(3)	107.0(2)	N(13)-C(14)-N(15)	106.4(2)	N(25)-C(26)-N(27)	106.4(2)	105.9(12)
C(2)-N(3)-C(4)	109.8(2)	C(14)-N(15)-C(16)	110.5(2)	C(26)-N(27)-C(28)	110.7(2)	110.7(5)
N(1)-C(2)-O(10)	126.2(2)	N(13)-C(14)-O(22)	125.6(2)	N(25)-C(26)-O(34)	126.3(2)	126.2(6)
N(3)-C(2)-O(10)	126.8(2)	N(15)-C(14)-O(22)	127.9(3)	N(27)-C(26)-O(34)	127.3(2)	127.8(10)
b) Substituents						
N(1)-C(11)	1.449(5)	N(13)-C(12)	1.455(3)	N(25)-C(24)	1.451(3)	
N(3)-C(23)	1.454(4)	C(11)-C(12)	1.520(5)	C(23)-C(24)	1.506(5)	
C(9)-N(1)-C(11)	126.0(2)	C(21)-N(13)-C(12)	126.1(2)	C(33)-N(25)-C(24)	126.1(2)	
C(2)-N(1)-C(11)	123.6(2)	C(14)-N(13)-C(12)	122.7(2)	C(26)-N(25)-C(24)	124.5(2)	
C(4)-N(3)-C(23)	126.3(2)	N(1)-C(11)-C(12)	111.8(3)	N(3)-C(23)-C(24)	112.9(2)	
C(2)-N(3)-C(23)	123.5(2)	N(13)-C(12)-C(11)	111.0(3)	C(23)-C(24)-N(25)	113.0(2)	

N15-C(14)-N(13)-C(12)	-168.1(2)	C(14)-N(13)-C(12)-C(11)	78.1(3)
N(13)-C(12)-C(11)-N(1)	57.6(3)	C(12)-C(11)-N(1)-C(2)	-90.8(3)
C(11)-N(1)-C(2)-N(3)	169.9(2)	N(1)-C(2)-N(3)-C(23)	-173.9(2)
C(2)-N(3)-C(23)-C(24)	-95.1(3)	N(3)-C(23)-C(24)-N(25)	-62.9(3)
C(23)-C(24)-N(25)-C(26)	105.4(3)	C(24)-N(25)-C(26)-N(27)	178.3(2)

c) Hydrogen interactions

D-H...A	D-H	D...A	H...A	D-H...A
N(15)-H(15)...O(10)(-x,-y,-z)	0.93(3)	2.833(3)	1.95(4)	156(4)
N(27)-H(27)...O(22)(x,½−y,½+z)	0.89(4)	2.799(3)	1.91(4)	176(4)
C(32)-H(32)...O(34)(-x,-½+y,½-z)	0.98(3)	3.314(3)	2.34(3)	177(3)
C-H···Centroid	C-H	C···Centr.	H···Centr.	C-H···Centr.
C(11)-H(112)...C(**A**)(½-x,½-y,½-z)	0.98(4)	3.565(3)	2.91(4)	125(3)
C(18)-H(18)...C(**B**)(-x,-½+y,½-z)	1.02(4)	3.814(3)	2.94(4)	144(2)
C(18)-H(18)...C(**C**)(-x,-½+y,½-z)	1.02(4)	3.527(4)	2.75(4)	133(3)

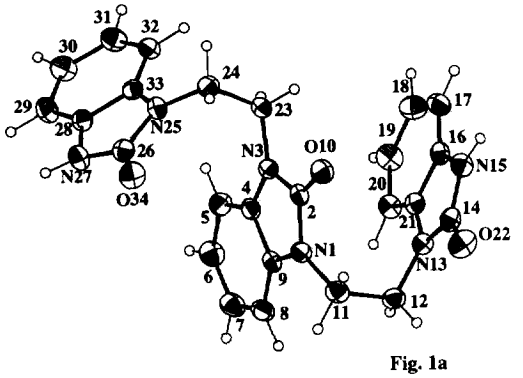


Fig. 1a

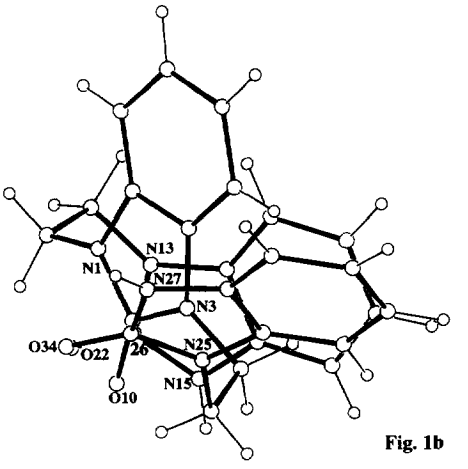


Fig. 1b

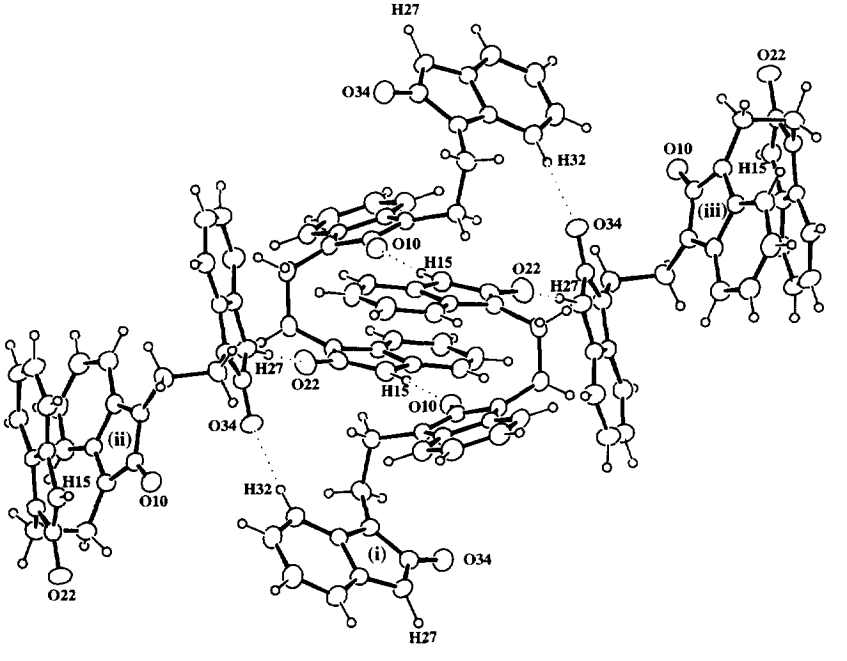


Fig. 1c

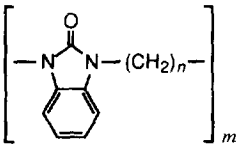
Fig. 1. (a) Molecular structure showing the atomic numbering and 30% probability ellipsoids. (b) Projection along the line joining the C(26) and C(14) atoms. (c) Hydrogen bonding scheme displaying the donor and acceptor groups (i=-x,-y,-z; ii=x,1/2-y,-1/2+z; iii=-x,-1/2+y,1/2-z).

with neither substituents in the benzene ring nor disorder and R < 0.010 (DRPRDL,[21] KAMCIK,[22] VUCFOO[23] and YILFUU[24]) apart from that of the 2,3-dihydrobenzimidazolin-2-one (ZEFXIR[25] and ZEFXIR01[26]). The average geometry is also gathered in Table 4 and it is in good agreement with that of the present work. The benzimidazolinone rings are significantly not planar (χ^2 = 247.01, 131.25 and 287.17 vs. the tabulated value of 12.60) and the angles that the central ring [N(1),..,C(9)] forms with the other two [N(13),.., C(21) and N(25),..., C(33)] are 25.6(1) and 54.4(1)° respectively giving rise to an almost helical conformation (Fig. 1b). Although pairs of benzene rings related by center of inversion (Fig. 1c) are parallel with an interplanar separation of 2.966(1) Å they are completely offset from each other, the distance between their centroids being 6.812(2) Å preventing any stack.

The inclusion of the ethylene chains which join two benzimidazolinone molecules drastically modify the crystal packing of the *N,N'*-unsubstituted molecules.[25-27] In compound **30**, the molecules are linked by one N(15)-H(15)···O(10) hydrogen bond into dimer units (Fig 1c and Table 4) through a symmetry center at (0,0,0) and the equivalent ones. Pairs of these dimers related by twofold screw axis and glide planes (ii and iii in Fig. 1c) are joined through the other N(27)-H(27)···O(22) bond and reinforced by C-H···O interactions to form a 2D network. Since four molecules per unit cell form this net, the I-body centring generates a second motif in which the dimers lie across the symmetry center at (1/4, 1/4, 1/4) and their symmetry related ones. Only weak C-H···π electronic cloud interactions are between both nets (Table 4). This crystal packing leads to a structure with no-accessible voids[28] and the total packing coefficient of 0.66 is rather low. There are no hydrogen interactions involving the disordered water molecule, the shortest distance being O(35)···H(6) = 3.39(5) Å.

CONCLUSIONS

Although cyclic tetramer **31** cannot be obtained in preparative yields by the methodologies we have used, we succeed in preparing trimer **30** and heptamer **32** which can be classified as *podands* (acyclic hosts).[29] Our methodology can be used for the controlled construction of *N,N'*-linked α,ω-alkanediyl-poly(benzimidazolin-2-ones), with the general structure:



where *m*, number of benzimidazolin-2-one units and *n*, alkyl chain length, can be varied as desired. In the present paper, we have reported the case *n* = 2, where elimination side-reactions are present in all steps.

EXPERIMENTAL SECTION

Synthesis.- IR spectra were recorded with a Perkin-Elmer PE-883 spectrometer. Mass spectra of the intermediate compounds were recorded on a SX102 type mass spectrometer (Jeol Ltd, Tokyo, Japan). Elemental analyses were determined with a Perkin-Elmer microanalyzer. Column chromatography was performed using silica gel Merck 60 (230-400 mesh) or neutral aluminium oxide (Merck 100-125 mesh). Benzimidazole **13**, benzimidazolin-2-one **14** and TBAB are commercial compounds; compound **15** was prepared according to ref. 2.

NMR Spectroscopy.- Most spectra were recorded on a Varian Unity 300 spectrometer.

Table 5. Crystal analysis parameters at room temperature.

Crystal data

Chemical formula	$C_{25}H_{22}N_6O_3.H_2O$	Crystal system	Monoclinic
Mr	472.50	Space group	*I2/a*
a (Å)	19.7316(25)	α (°)	90
b (Å)	11.8232(9)	β (°)	114.303(10)
c (Å)	22.5666(37)	γ (°)	90
Z	8	*Dx* (gr/cm³)	1.31
V (Å³)	4798.0(11)	Radiation	CuKα
Wavelength (Å)	1.5418	No. of reflections for	
θ range for lattice parameters (°)	2-45	lattice parameters:	53
Absorption coefficient (cm^{-1})	7.53	Crystal colour	Colorless
Crystal description	Prism	Crystal size (mm)	0.46 x 0.20 x 0.20

Data collection

Diffractometer type	Seifert XRD3000-S four circle diffractometer. Graphite oriented monocromator.		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θ_{max} (°)	65
No. of standard reflections (interval)	2 (90 min.). 4.8%decay	Scan width (°)	1.5
No. of independent reflections	3737	No. of observed reflections, I>2σ(I)	2516

Refinement

Treatment of hydrogen atoms	See experimental part	Refinement: Least-Squares on *Fo*. Full matrix	
Secondary extinction correction (10^4)	0.23(3)		
R	0.045	No. of parameters refined	404
wR	0.048	Degrees of freedom	2112
$(\Delta\rho)_{max}$ (e/Å³)	0.55	Ratio of freedom	6.2
<Shift/error>	0.02	Max. thermal value ($Å^2$)	U[O(351)]=0.24(1)

Weighting scheme: Empirical as to give no trends in $<\omega\Delta^2F>$ vs. <|Fobs|> and $<\sin\theta/\lambda>$.

Table 6. Final atomic coordinates and $Ueq=(1/3)\Sigma[Uij\cdot a_i^*\cdot a_j^*\cdot a_i\cdot a_j\cdot\cos(\mathbf{a}_i,\mathbf{a}_j)]$.

Atom	x	y	z	Ueq	Atom	x	y	z	Ueq
N(1)	0.6869(1)	0.6370(2)	0.6740(1)	0.043(1)	C(20)	0.6969(2)	0.3588(2)	0.6543(1)	0.047(1)
C(2)	0.6128(1)	0.6113(2)	0.6555(1)	0.040(1)	C(21)	0.6625(1)	0.4110(2)	0.5949(1)	0.040(1)
N(3)	0.6070(1)	0.5588(2)	0.7071(1)	0.040(1)	O(22)	0.6307(1)	0.5965(2)	0.4685(1)	0.066(1)
C(4)	0.6775(1)	0.5488(2)	0.7583(1)	0.042(1)	C(23)	0.5384(1)	0.5089(2)	0.7044(1)	0.045(1)
C(5)	0.7005(2)	0.5001(2)	0.8186(1)	0.050(1)	C(24)	0.4951(2)	0.5876(3)	0.7283(1)	0.048(1)
C(6)	0.7763(2)	0.5021(3)	0.8578(1)	0.058(1)	N(25)	0.5349(1)	0.6180(2)	0.7962(1)	0.043(1)
C(7)	0.8263(2)	0.5500(3)	0.8368(2)	0.058(1)	C(26)	0.5680(1)	0.7224(2)	0.8181(1)	0.047(1)
C(8)	0.8032(2)	0.5996(2)	0.7760(1)	0.051(1)	N(27)	0.5973(1)	0.7181(2)	0.8841(1)	0.050(1)
C(9)	0.7276(1)	0.5978(2)	0.7369(1)	0.040(1)	C(28)	0.5817(1)	0.6148(2)	0.9052(1)	0.042(1)
O(10)	0.5618(1)	0.6318(2)	0.60229(8)	0.050(1)	C(29)	0.5963(2)	0.5733(3)	0.9658(1)	0.056(1)
C(11)	0.7173(2)	0.6771(2)	0.6293(1)	0.050(1)	C(30)	0.5712(2)	0.4647(3)	0.9699(2)	0.059(1)
C(12)	0.7439(2)	0.5802(2)	0.6001(1)	0.049(1)	C(31)	0.5339(2)	0.4009(3)	0.9146(2)	0.057(1)
N(13)	0.6839(1)	0.5009(2)	0.56657(9)	0.042(1)	C(32)	0.5187(2)	0.4422(2)	0.8533(1)	0.048(1)
C(14)	0.6292(1)	0.5217(2)	0.5055(1)	0.045(1)	C(33)	0.5430(1)	0.5508(2)	0.8493(1)	0.040(1)
N(15)	0.5753(1)	0.4425(2)	0.4951(1)	0.048(1)	O(34)	0.5706(1)	0.8018(2)	0.7841(1)	0.060(1)
C(16)	0.5933(1)	0.3743(2)	0.5493(1)	0.042(1)	O(35)	0.731(1)	0.264(2)	0.9728(8)	0.239(10)
C(17)	0.5562(2)	0.2864(2)	0.5629(1)	0.052(1)	O(35')	0.679(1)	0.213(2)	0.924(1)	0.226(15)
C(18)	0.5905(2)	0.2353(3)	0.6228(2)	0.060(1)	pp[O(35)]=0.60(3), pp[O(35')]=0.40(3)				
C(19)	0.6593(2)	0.2700(2)	0.6677(2)	0.059(1)	pp= population parameter				

Mass Spectrometry.- Mass spectra were recorded on a SX102 type spectrometer (Jeol Ltd, Tokyo, Japan). Xenon was used in the FAB experiments. The energy of the neutral atom beam was 3 keV (emission current: 20 mA). Calibration was accomplished using Ultramark 1621 (Heraeus, Karlsruhe, Germany) as a reference. Samples were placed on a target after dissolving them directly in the matrix. Glycerol and *m*-nitrobenzyl alcohol were obtained from Aldrich.

X-ray Analysis.- The details of the X-ray data collection, structure solution and refinement are provided in Table 5. The structure was solved by direct methods (SIR92)[30] and refined by least-squares procedures on F_{obs}. The water molecule, located close a binary axis, appears to be disordered over two positions O(35) and O(35') with site occupation factors of 0.60(3) and 0.40(3) respectively. All hydrogen atoms except those of the water molecule were obtained from difference Fourier synthesis and included and refined isotropically in the last cycles. The scattering factors were taken from the *International Tables for X-Ray Crystallography*.[31] Table 6 list the final atomic coordinates and equivalent thermal factors for non-hydrogen atoms. The calculations were carried out with the XTAL3.4 System,[18] PESOS[32] and PARST[33] set of programs running on a DEC3000-300X workstation.

*1,2-Bis(benzimidazol-1-yl)ethane (**19**).*

The compound was prepared by liquid PTC following the procedure reported in ref. 13. Purification was performed by column chromatography on silica gel (50 g). Elution with dichloromethane/ethanol 9:1 afforded 70% of compound **19**, mp 225-226 °C, lit. mp 216-220 °C.[13]

*Bis(2-bromoethyl)-1,2-bis(benzimidazol-1-ium)ethane dibromide (**20**).*

A suspension of **19** (520 mg, 2.24 mmol) in 5 mL of 1,2-dibromoethane was refluxed for 72 h resulting in a black precipitate. The solid was filtered off, dissolved in water, treated by charcoal, filtered and the clear solution evaporated affording 0.37 g (26 %) of **20** as a white solid mp > 300 °C (from methanol). ^{1}H NMR (DMSO-d_6) δ 5.18 (4H, s, A_4 system), 4.93 and 3.95 (8H, t, AA'BB' system, J_{AB} = 5.7 Hz), 7.66 (4H, m, H5 and H6), 8.14 (t, 2H, H4) and 7.95 (t, 2H, H7) and 9.8 (2H, s, H2). ^{13}C NMR (DMSO-d_6) δ 30.79 (CH_2Br), 45.79 (CH_2CH_2Br), 48.14 (CH_2CH_2), 129.00 and 130.76 (C5 and C6), 112.95 and 113.56 (C4 and C7), 143.22 (C2). Anal. calcd for $C_{20}H_{22}N_4Br_4$: C, 37.65%; H, 3.48%, N, 8.78%. Found: C, 37.38%; H, 3.54%, N, 9.08%.

*Reaction of **20** with triethylamine and air.*

Compound **20** (0.35 g, 0.55 mmol) was dissolved in freshly distilled acetonitrile (70 mL). Triethylamine (2.1 mL, 14 mmol) was added and the resulting solution was stirred for 7 days at r.t. Afterwards, water (175 mL) and 35% hydrochloric acid (17.5 mL) were added and the acid solution was extracted with $CHCl_3$ (3 x 50 mL) and the solution was boiled with charcoal and filtered. By evaporation, 80 mg of a solid was obtained. Column chromatography ($CHCl_3$/ethanol 8:2) yields a mixture of compounds **23** (34 %) and **24** (28 %).

*Reaction of **20** with sodium hydride and air.*

Compound **20** (0.1 g, 0.16 mmol) was mixed with NaH (0.1 g, 4 mmol) in anhydrous acetonitrile (20 mL). After 5 min of stirring the white solution turns yellow; the stirring was maintained for 2 h at r.t. in the open. Then, the solvent was removed and the residue was extracted with chloroform. The dark solution was refluxed 10 min with charcoal. The solution was filtered, the solvent evaporated off and the residue washed with hexane to afford 40 mg of 1,2-[bis(2-oxo-3-vinylbenzimidazolin-1-yl]ethane **25** were obtained (90 %), mp 165-167 °C (from dichloromethane-hexane).

*Reaction of benzimidazolin-2-one (**14**) with 1,2-dichloroethane.*

1.- Benzimidazolin-2-one (3.35 g, 25 mmol), finely ground potassium hydroxide (4.2 g, 75 mmol) and water (1 mL) were stirred at room temperature for 1 h. 1,2-Dichloroethane (50 mL) and TBAB (240 mg, 0.75 mmol) were added and the mixture heated slowly to the final temperature to minimize the elimination reaction (4h to 50 °C, 2.5 h to 80 °C and 2h to 100 °C). The mixture was filtered off and the residue was washed with dichloromethane. The residue was dissolved in 1,2-dichloroethane (50 mL) and the stirring continued at 100 °C for 4 h. The mixture was filtered off and the combined organic solutions were dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (50 g). Elution with dichloromethane afforded successively 3.75 g of 1,3-bis(2-chloroethyl)benzimidazolin-2-one **17** (58 %), mp 130-132 °C, 1,2-bis[3-(2-chloroethyl)benzimidazolin-2-one] **22** (60 mg, 1.1 %) mp > 300 °C and 1-[3-(2-chloroethyl)-2-oxobenzimidazol-1-yl]-2-(2-oxobenzimidazol-1-yl)ethane **21** (100 mg, 2.2 %). Anal. calcd. for **17** ($C_{11}H_{12}N_2Cl_2O$): C, 50.97 %; H, 4.67 %; N, 10.80 %. Found: C, 51.26 %; H, 4.87 %; N, 10.78 %. Anal. calcd. for **21** ($C_{18}H_{17}N_4ClO_2$): C, 60.59 %; H, 4.80 %; N, 10.80 %. Found: C, 51.26 %; H, 4.87 %; N, 10.78 %. Anal. calcd. for **22** ($C_{20}H_{20}N_4Cl_2O_2$): C, 57.29 %; H, 4.81 %; N, 16.91 %. Found: C, 57.19 %; H, 4.95 %; N, 17.00 %.

2.- Similarly, but extending the reaction time to 48 h at room temperature after the first addition of 1,2-dichloroethane and to 4 h at 100 °C after the second addition of 1,2-dichloroethane. The mixture was filtered off and the combined organic solutions were dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (50 g). Elution with ethyl acetate afforded 2.1 g of **17** (32.4 %) and 1-(2-chloroethyl)benzimidazolin-2-one **16** (100 mg, 2 %), mp > 300 °C. Compound **16** is unstable and do not give good analytical results, it was characterized by ^1H and ^{13}C NMR.

3.- Similarly, but extending the reaction time to 15 h at room temperature after the first addition of 1,2-dichloroethane and to 2h at 100 °C after the second addition of 1,2-dichloroethane. The mixture was filtered off and the combined organic solutions were dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (50 g). Elution with dichloromethane afforded 2.35 g of **17** (36.3 %), **22** (560 mg, 10.7 %) and 1,3-bis-{2-[3-(2-chloroethyl)-2-oxobenzimidazol-1-yl]ethyl}-2-oxobenzimidazole **28** (340 mg, 7.1 %). Cyclic tetramer **31** was isolated in very small amounts, about 1% and characterized only by MS. Anal. calcd. for **28** ($C_{29}H_{28}N_6Cl_2O_3$): C, 60.11 %; H, 4.87 %; N, 14.50 %. Found: C, 59.23 %; H, 4.99 %; N, 14.62 %.

*1,3-Bis-{2-(3-isopropenyl-2-oxobenzimidazol-1-yl)ethyl}-2-oxobenzimidazole (**29**).*

1.- In a two necked flask a mixture of 1-isopropenylbenzimidazolin-2-one **15** (350 mg, 2 mmol), potassium hydroxide (123 mg, 2.2 mmol) and TBAB (10 mg, 0.03 mmol) in toluene (10 mL) was heated to 100 °C for 30 min. At this temperature, a suspension of **17** (260 mg, 1 mmol) in toluene (5 mL) was added and the reaction was heated to reflux for 48 h. The reaction was filtered off and the residue washed with toluene (10 mL). Drying over anhydrous magnesium sulfate and removal of the solvent afforded the crude product which was purified by column chromatography on silica gel (40 g). Elution with dichloromethane afforded 50 mg of starting material **17**. Elution with dichloromethane:ethyl acetate 8:2 afforded 1-(3-isopropenyl-2-oxobenzimidazol-1-yl)-2-(3-vinyl-2-oxobenzimidazol-1-yl)ethane **27** (30 mg, 8%) mp 101-103 °C (from etharhexane) and 1-[3-(2-chloroethyl)2-oxobenzimidazol-1-yl)-2-(3-isopropenyl-2-oxobenzimidazol-1-yl)ethane] **26** (10 mg, 2.5 %) mp 95-97 °C. Finally, elution with ethyl acetate afforded the trimer 1,3-bis-{2-(3-isopropenyl-2-oxobenzimidazol-1-yl)ethyl}-2-oxobenzimidazole **29** (30 mg, 8.4 %) mp 122-124 °C. Anal. calcd. for **26** ($C_{21}H_{21}N_4ClO_2$): C, 63.55 %; H, 5.33 %; N, 14.12 %. Found: C, 63.31 %; H, 5.42 %; N, 14.11 %.

2.- A mixture of 1-isopropenylbenzimidazolin-2-one **15** (700 mg, 4 mmol), 1,3-bis(2-chloroethyl)-benzimidazolin-2-one **17** (520 mg, 2 mmol) and potassium hydroxide (240 mg, 4.4 mmol) was irradiated in a microwave oven at 780 W for 22 min. (final temperature 167 °C). The crude product was washed with dichloromethane (20 mL) and the organic solution was dried over anhydrous magnesium sulfate. Removal of the solvent and column chromatography on silica gel (50 g), using chloroform:ethyl acetate 8:2 as eluent afforded 1,3-divinylbenzimidazolin-2-one **18** as an oil (20 mg, 2.7 %). Elution with chloroform:ethyl acetate 1:1 afforded **27** (310 mg, 43 %) and finally, elution with ethyl acetate afforded **29** (350 mg, 49.1 %), mp 122-124 °C. Anal. calcd. for **18** ($C_{11}H_{10}N_2O$): C, 70.95 %; H, 5.41 %; N, 15.04 %. Found: C, 71.13 %; H, 5.77 %; N, 14.93 %. Anal. calcd. for **27** ($C_{21}H_{20}N_4O_2$): C, 69.98 %; H, 5.59 %; N, 15.55 %. Found: C, 70.33 %; H, 5.78 %; N, 15.35 %.

3.- In a round bottom flask provided with a reflux condenser, potassium carbonate (8.28 g, 60 mmol) and tetrabutylammonium bisulfate (210 mg, 0.6 mmol) were added to a solution of 1-isopropenylbenzimidazolin-2-one **15** (1.05 g, 6 mmol) and 1,3-bis(2-chloroethyl)benzimidazolin-2-one **17** (780 mg, 3 mmol) and the solution was heated to reflux for 15 h. Inorganic salts were removed by filtration and washed with boiling acetonitrile. The combined organic solutions were evaporated to dryness, dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent removed in vacuum. The crude product was purified as indicated before in 2, affording **18** (10 mg, 0.9 %), **27** (230 mg, 21.3 %) and the trimer **29** (830 mg, 77.6 %). Anal. calcd. for **29** ($C_{31}H_{30}N_6O_3$): C, 69.65 %; H, 5.66 %; N, 15.72 %. Found: C, 69.53 %; H, 5.67 %; N, 15.99 %.

*1,3-Bis-{2-(2-oxobenzimidazol-1-yl)ethyl}-2-oxobenzimidazole (**30**).*

35 % Hydrochloric acid (3.4 mL) was added to a solution of **29** (670 mg, 1.25 mmol) in methanol:water 1:1 (10 mL) and the mixture was heated to reflux for 1 h. A white solid that precipitates was identified as the trimer **30** (510 mg, 89.5 %) mp 294-296 °C (methanol). Anal. calcd. for $C_{25}H_{28}N_6O_3$: C, 66.07 %; H, 4.88 %; N, 18.49 %. Found: C, 65.85 %; H, 4.94 %; N, 18.05 %.

*1,3-Bis-{2-(3-(2-{3-[2-(2-oxobenzimidazol-1-yl)ethyl)}-2-oxobenzimidazol-1-yl]ethyl}-2-oxobenzimidazol-1-yl)-ethyl-2-oxobenzimidazole (**32**).*

A solution of **30** (300 mg, 0.66 mmol), sodium hydride (70 mg, 1.76 mmol) in DMF (50 mL) was heated to 90 °C for 2 h. Lithium bromide (120 mg, 1.38 mmol) was added and the stirring was continued for 15 min. At this time a solution of 1,3-bis(2-chloroethyl)benzimidazolin-2-one (165 mg, 0.66 mmol) in DMF (10 mL) was added during 20 min and the reaction was continued at 90 °C for 24 h. The reaction was poured into ice and the solid was filtered. The solid was chromatographed on silica gel using dichloromethane:methanol:acetone 5:1:1 as eluent. Compound **32** was purified by preparative TLC using dichloromethane:methanol:acetone 10:1:1 (83 mg, 23 %), mp 175-180 °C (dec.).

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