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Synthesis, Structure and Properties of Pyrazole Type Tetrakis Compounds

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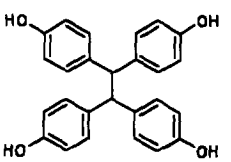
Dedicated to Prof. Dr. Hans Suschitzky on the occasion of his 80th birthday

Abstract: A series of pyrazole type tetrakis compounds has been synthesized by reaction of aromatic or heterocyclic dialdehydes and pyrazolone derivatives. Structure and tautomerism of the products were investigated by spectroscopic methods and X-ray analysis. Several tetrakis compounds form inclusion complexes with solvents like alcohols, ethers, and ketones in a definite ratio via hydrogen bonds.

Introduction

The use of crystalline inclusion compounds in separation, stabilisation and selection of chemical species, in topochemistry, or in the developement of new solid materials became apparent in the past years.[1] A great variety of organic hosts which form different types of host-guest complexes has been synthesized and studied to clarify the interaction between host and guest at the molecular level.[2] Thereby interactions by means of hydrogen bridges offer the possibility of constructing solids with a definite molecular pattern.[3] It was found that host design based on phenolic species as simple building blocks is very useful.[4] Recently, it has been published that 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane (**1**) exhibits highly selective inclusion behaviour towards various n-donors.[5]



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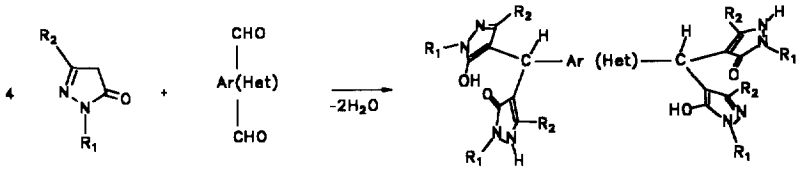
It was now our interest to investigate the inclusion ability of comparable tetrakis compounds wherein the phenolic units are substituted by pyrazolone molecules.

Results and Discussion

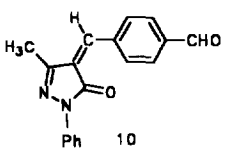
The following series of pyrazole type tetrakis compounds was synthesized by reaction of aromatic or heterocyclic dialdehydes and an excess of an appropriate pyrazolone derivative.



2 3 4 - 9

	R^1	R^2	Ar (Het)
4a	C_6H_5	CH_3	
4b	C_6H_5	CH_3	
5a	C_6H_5	CH_3CONH	
5b	C_6H_5	CH_3CONH	
6a		CH_3	
6b		CH_3	
7a		CH_3	
7b		CH_3	
8	C_6H_5	CH_3	
9	C_6H_5	CH_3	

In all cases the formation of 4:1-products is preferred to a great extent independent of the solvent. Using the pyrazolone **2** ($R^1 = C_6H_5$, $R^2 = CH_3$) and terephthaldialdehyde, isophthaldialdehyde or terephthaldialdehyde monodiethyl acetal in different stoichiometric ratios also 1:1- **(10)** and 2:1- **(11 and 12)** reaction products could be isolated, but there was no indication to the formation of 3:1-reaction products.



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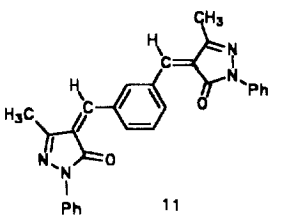

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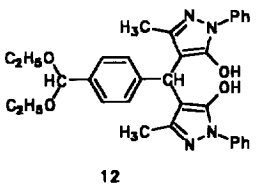

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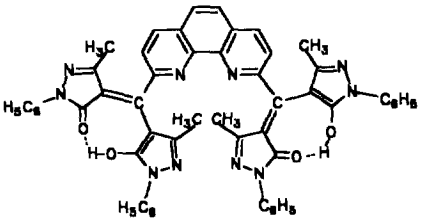
Corresponding to similar monocondensation products of pyrazolones and aldehydes **10** and **11** exist in (Z)-configuration.[6]

Synthesis of **9** succeeded only in methanol and an inert gas atmosphere (dry nitrogen). Otherwise, in the presence of oxygen the intensively yellow coloured oxonole **13** was formed.



13

However, the oxonole **13** could easily be reduced to **9** by catalytic hydrogenation.
Structurally related compounds with unusual formation of a strong chelated hydrogen bond in an eight-membered ring have already been investigated by *HÄNSEL*.[7]

Attempts to form the inclusion complexes of **4** - **7** were carried out by recrystallization from various solvents. After product separation and careful drying in vacuum the host-guest ratios were determined by proton NMR integration. All compounds incorporated solvent molecules, but the best results were obtained with **4a** and **4b** . They are summarized in table 1.

Table 1. Molar host-guest ratios of inclusion complexes from **4a** and **4b**

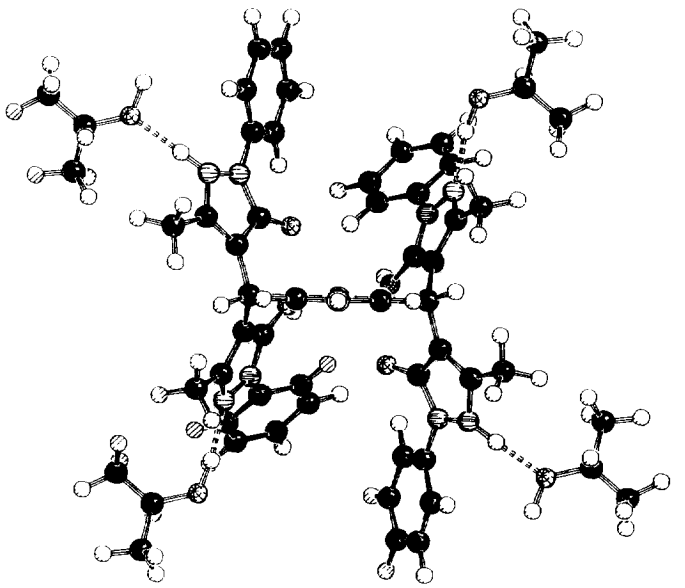
	guest	molar ratio
	methanol	1:2
	ethanol	1:2
	2-propanol	1:2
4a	tetrahydrofuran	1:2
	1,4-dioxane	1:2
	acetone	1:1
	methyl ethyl ketone	1:1
	methanol	1:1
4b	ethanol	1:1
	1,4-dioxane	1:2

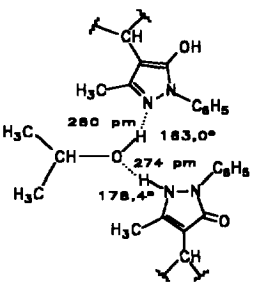
Solvent free **4a** (synthesized in chloroform) also incorporates low boiling solvents from the gas phase. Additionally, in this way it was possible to get inclusion complexes with triethylamine, whereas recrystallization of **4a** from triethylamine led to decomposition.

To investigate selectivity, **4a** was recrystallized from two-component solvent mixtures. If there is any selectivity the host compound should preferably combine with only one component. Study of the results showed

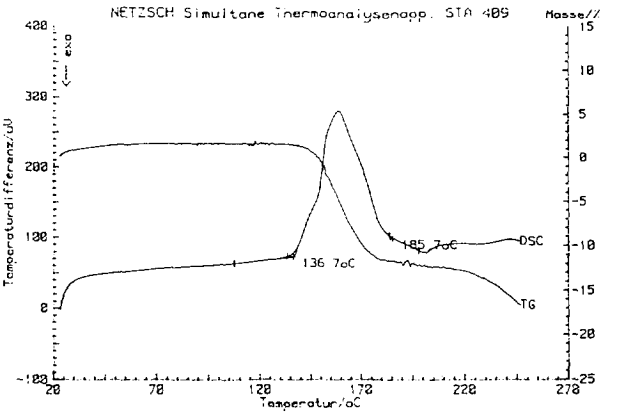
that such a highly selective inclusion behaviour does not occur. A certain selectivity was only observed in the case of cyclic ethers like dioxane and tetrahydrofuran.

An X-ray crystal structure of the inclusion complex of **4a** with 2-propanol shows that the host molecule has C_2-symmetry in the solid state. In each case two pyrazole rings of the tetrakis compound exist as NH- and OH-tautomers. Bond lengths and angles are in good agreement with data obtained for the separate pyrazoles.[8] Every host molecule is connected with two neighbouring molecules by the hydroxy group of the 2-propanol. Both, the oxygen and the hydrogen atom of the hydroxy group are incorporated into hydrogen bonds with different pyrazole units. The O···H-N distance is 274 pm with an angle of 178° between these three atoms, while the O-H···N distance is 280 pm with an angle of 163°. The connection of the tetrakis compounds via 2-propanol molecules causes the formation of chains in the crystal. Complete lists with bond lengths and atomic coordinates have been deposited.



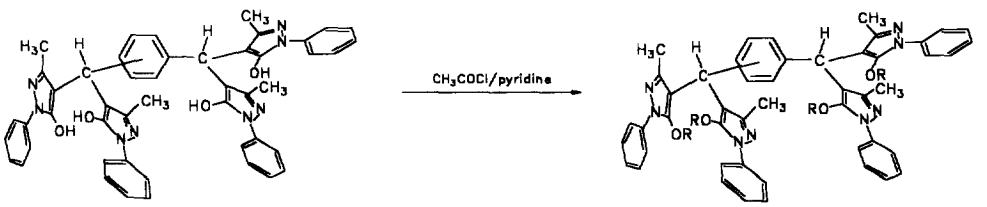


From the inclusion complex of **4a** with 2-propanol we also carried out a Differential Thermal Analysis (DTA) and a Thermal Gravimetrical Analysis (TGA). It can be concluded that the complex released the 2-propanol molecules in a single step between 137°C and 186°C. The difference compared to the boiling point of 2-propanol (82°C) is remarkable. The observed weight loss is in good agreement with the required stoichiometry. The thermograms for other inclusion complexes resemble this.



NMR investigations show that the inclusion complexes were probably destroyed in DMSO-d_6 solution. There are no significant shift differences between solvent free tetrakis compounds and the derived inclusion complexes. From ^1H and ^{13}C chemical shifts it can be concluded that the tetrakis compounds in DMSO-d_6 exist nearly exclusively as OH-tautomers in contrast to the solid state.[9]

Selective O-acylation of **4a,b** i.e. with acetyl chloride in pyridine gave the corresponding tetraacetyl compounds **14a,b** in moderate yields.



4a,b

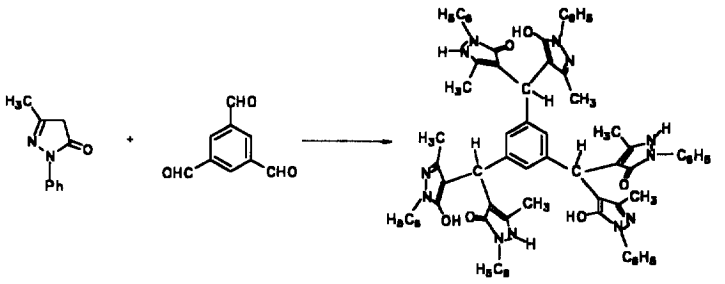
14a,b : R=CH_3CO

It was impossible to get inclusion complexes from the tetraacyl compounds. It means that the tautomeric system of the pyrazoles is essential for the formation of hydrogen bonds in the described chain like inclusion complexes.

Recently, patterns of hydrogen bonds between specific functional groups in molecular crystals have been identified and rules have been proposed for their formation.[10]

The bonding conditiones of the tetrakis compounds with regard to alcoholes should differ from those with regard to the ethers and ketones. Unfortunately, it was not possible to get an X-ray crystal structure from such inclusion complexes. Therefore, it can not be excluded that besides formation of hydrogen bonds also an inclusion of solvent guest molecules in discrete pockets (cage type inclusion complexes) is of importance.

The reaction of pyrazolone **2** ($R^1 = C_6H_5$, $R^2 = CH_3$) with benzene-1,3,5-tricarbaldehyde in ethanol gave the corresponding hexakis compound **15** in good yield.



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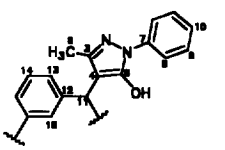
With **15** no inclusion of solvents and formation of three-dimensional networks of hydrogen-bonded molecules was observed.

Experimental

General experimental procedures: Melting points were determined on a BOETIUS melting point apparatus. Elemental analyses were obtained by an analyzer CHN-O-Rapid (Fa. Heraeus). IR spectra were measured as KBr pellets with a UR-20 spectrometer (Carl-Zeiss-Jena), while UV/VIS spectra were recorded with a DU-650 (Fa. Beckman). The ^1H and ^{13}C NMR spectra were recorded with a VARIAN GEMINI-200 (^1H: 199.975 MHz, ^{13}C: 50.289 MHz) and a VARIAN UNITY-400 (^1H: 399.952 MHz, ^{13}C: 100.630 MHz), respectively; δ = 7.26 for chloroform, 2.51 for DMSO-d_6 as internal standard.
Mass spectra were obtained with a VARIAN VG 12-250 (EI^+), VG ZAB HSQ (FAB), and a Bio-ion Bin 10k plasma desorption instrument (Bio-ion AB/PDMS). TGA/DTA analyses were run with a PERKIN ELMER TGA-7 and a Netzsch STA 409. The X-ray structure was determined on a diffractometer STOE STADI 4.

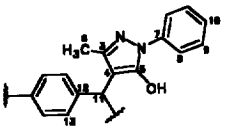
*General procedure for synthesis of **4-9**:* To a solution of 1 mmol dialdehyde in chloroform 4 mmol of the corresponding pyrazolone derivative was added. Stirring and refluxing gave a colour change from slightly yellow to orange-red, which disappeared during further reaction. The products were separated directly from the reaction mixture or were obtained by evaporation of the solvent. Purification by recrystallization or chromatography gave nearly colourless products.

Bis-1,3-[di-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]benzene (4a):



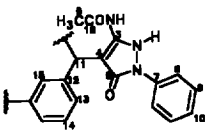
mp 190-194°C; ^1H NMR (200 MHz, DMSO-d_6) δ: 2.26 (s, 12H, CH_3), 4.88 (s, 2H, CH), 7.05-7.31 (m, 4H, phenyl-p-CH; 3H, isophthal-CH), 7.43 (dd, 8H, phenyl-m-CH), 7.69 (d, 8H, phenyl-o-CH), 14.08 (s, OH); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 11.87 (C^6), 33.72 (C^{11}), 104.77 (C^4), 120.99 (C^8), 124.96, 125.77 (C^{10}), 126.67, 128.22, 129.11 (C^9), 137.70 (C^7), 142.78 (C^{12}), 146.60 (C^3), 157.50 (C^5). Anal. Calcd. for $C_{54}H_{58}N_8O_6$: C, 70.87; H, 6.39; N, 12.24. Found: C, 70.44; H, 6.63; N, 12.37 (*2 $(CH_3)_2CHOH$). MS (PDMS): $^m/_z$ = 795 (M^+ + H).

Bis-1,4-[di-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]benzene (4b):



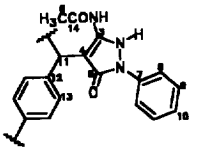
mp 218-220°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.31 (s, 12H, CH_3), 4.91 (s, 2H, CH), 7.21 (s, 4H, terephthal-CH), 7.25 (dd, 4H, phenyl-p-CH), 7.43 (m, 8H, phenyl-m-CH), 7.74 (m, 8H, phenyl-o-CH), 14.10 (s, OH); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 11.90 (C^6), 33.12 (C^{11}), 105.10 (C^4), 120.92 (C^8), 125.83 (C^{10}), 127.28 (C^{13}), 129.15 (C^9), 137.72 (C^7), 140.30 (C^{12}), 146.52 (C^3), 157.80 (C^5). Anal. Calcd. for $C_{48}H_{42}N_8O_4$: C, 71.41; H, 5.75; N, 13.33. Found: C, 70.87; H, 5.80; N, 13.47 (* C_2H_5OH). MS (PDMS): $^m/_z$ = 795 (M^+ + H).

Bis-1,3-[di-(3-acetamido-5-hydroxy-1-phenyl-pyrazol-4-yl)methyl]benzene (5a):



mp 209-211°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.15 (s, 12H, CH_3), 5.48 (s, 2H, CH), 7.03-7.32 (m, 4H, phenyl-p-CH; 3H, isophthal-CH), 7.42 (dd, 8H, phenyl-m-CH), 7.60 (d, 8H, phenyl-o-CH), 10.71 (s, NH); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 23.42 (C^6), 31.33 (C^{11}), 96.43 (C^4), 121.93 (C^8), 125.21, 126.10, 126.28 (C^{10}), 128.04, 129.04 (C^9), 136.91 (C^7), 141.65 (C^{12}), 144.87 (C^3), 158.36 (C^5), 169.89 (C^{16}). MS: Calcd. for $C_{52}H_{46}N_{12}O_8$, 967.02. Found (FAB): $^m/_z$ = 967 (M^+), 750 (M^+ - 1 pyrazole), 533 (M^+ - 2 pyrazole), 491 (M^+ - 2 pyrazole - H_2C=C=O).

Bis-1,4-[di-(3-acetamido-5-hydroxy-1-phenyl-pyrazol-4-yl)methyl]benzene (5b):



mp 213-215°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.18 (s, 12H, CH_3), 5.32 (s, 2H, CH), 7.10 (s, 4H, terephthal-CH), 7.28 (dd, 4H, phenyl-p-CH), 7.46 (dd, 8H, phenyl-m-CH), 7.64 (d, 8H, phenyl-o-CH), 10.58 (s, NH); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 23.40 (C^6), 30.93 (C^{11}), 96.97 (C^4), 121.63 (C^8), 126.21 (C^{10}), 127.10 (C^{13}), 129.12 (C^9), 137.17 (C^7), 139.38 (C^{12}), 144.84 (C^3), 158.22 (C^5) 169.92 (C^{14}). Anal. Calcd. for $C_{52}H_{46}N_{12}O_8$: C, 64.59; H, 4.79; N, 17.38. Found: C, 64.71; H, 4.67; N, 17.12.

Bis-1,3-[di-(5-hydroxy-3-methyl-1-(pyrid-2-yl)-pyrazol-4-yl)methyl]benzene (6a):

mp 161-166°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.07 (s, 12H, CH_3), 5.24 (s, 2H, CH), 6.99 (dd, 4H, pyridyl-CH), 7.18-7.42 (m, 4H, isophthal-CH), 7.72 (dd, 4H, pyridyl-CH), 7.87 (d, 4H, pyridyl-CH), 8.09 (d, 4H, pyridyl-CH); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 13.98 (C^6), 34.32 (C^{11}), 102.80 (C^4), 112.33, 119.76, 126.60 (C^{13}), 128.22 (C^{15}), 128.96 (C^{14}), 139.83, 141.67 (C^{12}), 145.78, 151.27 (C^3), 153.96 (C^5), 155.06. MS: Calcd. for $C_{44}H_{38}N_{12}O_4$, 798.87. Found (PDMS): $^m/_z$ = 799 (M^+).

Bis-1,4-[di-(5-hydroxy-3-methyl-1-(pyrid-2-yl)-pyrazol-4-yl)methyl]benzene (6b):

mp 263-268°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.07 (s, 12H, CH_3), 5.00 (s, 2H, CH), 7.18 (s, 4H, terephthal-CH), 7.20 (dd, 4H, pyridyl-CH), 7.85 (dd, 4H, pyridyl-CH), 8.20 (d, 4H, pyridyl-CH), 8.38 (d, 4H, pyridyl-CH). Anal. Calcd. for $C_{44}H_{38}N_{12}O_4$: C, 66.15; H, 4.79; N, 21.04. Found: C, 65.76; H, 4.83; N, 20.87. MS (PDMS): $^m/_z$ = 799 (M^+).

Bis-1,3-[di-(1-(1,3-benzothiazol-2-yl)-5-hydroxy-3-methyl-pyrazol-4-yl)methyl]benzene (7a):
mp 219-223°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.14 (s, 12H, CH_3), 5.12 (s, 2H, CH), 7.29 (d, 2H, isophthal-CH), 7.39 (dd, 4H, benzothiazolyl-CH; 1H, isophthal-CH), 7.44 (s, 1H, isophthal-CH), 7.47 (dd, 4H, benzothiazolyl-CH), 7.87 (d, 4H, benzothiazolyl-CH), 7.96 (d, 4H, benzothiazolyl-CH), 12.58 (s, 4H, OH). MS: Calcd. for $C_{52}H_{38}N_{12}O_4S_4$, 1023.09. Found (EI$^+$): $^m/_z$ = 792 (M$^+$ - 1 pyrazole), 561 (M$^+$ - 2 pyrazole).

Bis-1,4-[di-(1-(1,3-benzothiazol-2-yl)-5-hydroxy-3-methyl-pyrazol-4-yl)methyl]benzene (7b):
mp 235-240°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.20 (s, 12H, CH_3), 5.13 (s, 2H, CH), 7.36 (s, 4H, terephthal-CH), 7.45 (dd, 4H, benzothiazolyl-CH), 7.56 (dd, 4H, benzothiazolyl-CH), 7.93 (d, 4H, benzothiazolyl-CH), 8.17 (d, 4H, benzothiazolyl-CH), 12.60 (s, 4H, OH). MS: Calcd. for $C_{52}H_{38}N_{12}O_4S_4$, 1023.09. Found (EI$^+$): $^m/_z$ = 1022 (M$^+$).

Bis-2,6-[di-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]pyridine (8):
mp 223-226°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.20 (s, 12H, CH_3), 5.17 (s, 2H, CH), 7.24 (dd, 4H, phenyl-p-CH), 7.35 (d, 2H, pyridyl-CH), 7.45 (dd, 8H, phenyl-m-CH), 7.73 (d, 8H, phenyl-o-CH), 7.80 (dd, 1H, pyridyl-CH). MS: Calcd. for $C_{47}H_{41}N_9O_4$, 795.90. Found (FAB): $^m/_z$ = 796 (M$^+$), 622 (M$^+$ - pyrazole), 448 (M$^+$ - 2 pyrazole).

Bis-2,9-[di-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]-1,10-phenanthroline (9):
mp 231-234°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.24 (s, 12H, CH_3), 5.62 (s, 2H, CH), 7.29 (dd, 4H, phenyl-p-CH), 7.48 (dd, 8H, phenyl-m-CH), 7.75 (d, 8H, phenyl-o-CH), 7.99 (s, 2H, phenanthroline-CH), 8.11 (d, 2H, phenanthroline-CH), 8.57 (d, 2H, phenanthroline-CH). MS: Calcd. for $C_{54}H_{44}N_{10}O_4$, 897.01. Found (FAB): $^m/_z$ = 897 (M$^+$).

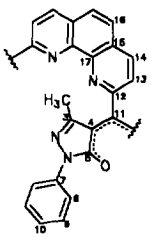
4-(4-Formylbenzyliden)-3-methyl-5-oxo-1-phenyl-4,5-dihydropyrazole (10):
1.74 g (10 mmol) of 5-Hydroxy-3-methyl-1-phenyl-pyrazole and 1.34 g (10 mmol) of terephthaldialdehyde were mixed and heated in a beaker. An intensively red-coloured melt was formed under development of steam. After 10 minutes the melt was cooled down and treated with ethanol. Recrystallization from ethanol gave red-coloured crystals.
mp 147-149°C; IR : 1675 (CO), 1690 (CHO); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.36 (s, 3H, CH_3), 7.20 (dd, 1H, phenyl-p-CH), 7.39 (s, 1H, =CH), 7.42 (dd, 2H, phenyl-m-CH), 7.94 (d, 2H, phenyl-o-CH), 7.98 (d, 2H, terephthal-CH), 8.58 (d, 2H, terephthal-CH), 10.09 (s, 1H, CHO); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 13.74 (CH_3), 119.55 (C^8), 125.64 (C^{10}), 129.32 (C^9), 130.04, 134.11, 138.26, 138.55, 138.74, 144.81 (=CH), 150.98 (C^3), 161.80 (C^5), 191.91 (CHO). MS: Calcd. for $C_{18}H_{14}N_2O_2$, 290.31. Found (EI$^+$): $^m/_z$ = 290 (M$^+$).

Bis-1,3-(3-methyl-5-oxo-1-phenyl-4,5-dihydropyrazol-4-ylidenmethinyl)benzene (11):
1.74 g (10 mmol) of 5-Hydroxy-3-methyl-1-phenyl-pyrazole and 0.67 g (5 mmol) of isophthaldialdehyde were dissolved in 40 mL of acetic acid containing 1 g of sodium acetate. After refluxing for 15 minutes an orange solid separated. After cooling the product was isolated and recrystallized from acetic acid.

mp 217-221°C; UV/VIS: 331 nm (lg ε = 4,76); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.38 (s, 6H, CH_3), 7.21 (dd, 2H, phenyl-p-CH), 7.39 (s, 2H, CH=), 7.45 (dd, 4H, phenyl-m-CH), 7.66 (dd, 1H, isophthal- CH), 7.95 (d, 4H, phenyl-o-CH), 8.78 (d, 2H, isophthal-CH), 9.39 (s, 1H, isophthal-CH). MS: Calcd. for $C_{28}H_{22}N_4O_2$, 446.51. Found (EI^+): $^m/_z$ = 446 (M^+).

1-[Bis-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]-4-diethoxymethyl-benzene (12):
mp 143-147°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.19 (t, 6H, CH_3), 2.05 (s, 6H, CH_3), 3.56 (m, 4H, CH_2), 4.73 (s, 1H, CH), 5.41 (s, 1H, CH), 7.08-7.52 (m, 14H, aryl-CH). Anal. Calcd. for $C_{32}H_{34}N_4O_4$: C, 71.35; H, 6.36; N, 10.40. Found: C, 71.52; H, 6.11; N, 10.58. MS (EI^+): $^m/_z$ = 534 (M^+ - 4H), 446 (M^+ - 2 ethanol).

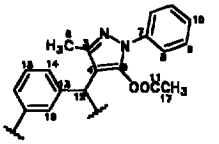
Oxonol 13:



mp 243-245°C; UV/VIS ($CHCl_3$,, nm): λ_{max} (lg ε) 402 (4,60), 335 sh (4,34), 305 sh (4,50), 283 sh (4,58), 252 (4,76); ^{1}H NMR (200 MHz, C_6D_6) δ: 1.31 (s, 12H, CH_3), 6.93 (dd, 4H, phenyl-p-CH), 7.03 (d, 2H, phenanthroline-CH), 7.13 (dd, 8H, phenyl-m-CH), 7.36 (s, 2H, phenanthroline-CH), 7.55 (d, 2H, phenanthroline-CH), 8.13 (d, 8H, phenyl-o-CH); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 16.66 (CH_3), 113.89 (C^4), 121.01 (C^8), 126.49 (C^{10}), 126.94 (C^{13}), 128.57 (C^{16}), 129.33 (C^9), 129.87 (C^{15}), 137.49 (C^7), 138.11 (C^{14}), 145.90 (C^{17}), 151.09 (C^{12}), 154.54 (C^{11}), 158.68 (C^3), 162.05 (C^5). Anal. Calcd. for $C_{54}H_{40}N_{10}O_4$: C, 72.63; H, 4.52; N, 15.69. Found: C, 72.35; H, 4.85; N, 15.46. MS (FAB): $^m/_z$ = 894 (M^+ + H).

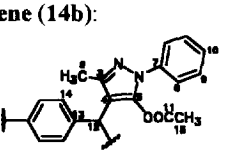
*Acetylation of **4a,b**:* 0.5 mmol of tetrakis compound **4a** or **4b** were dissolved in 15 mL of dry pyridine and dropwise treated with 3 mmol of acetyl chloride. Then the mixture was heated for 30 minutes at 50°C. After cooling the mixture was poured into ice-water containing HCl. The precipitate was collected, washed several times with 1N HCl and water. The product was purified by column chromatography (Kieselgel 60, eluent chloroform).

Bis-1,3-[di-(3-methyl-5-methylcarbonyloxy-1-phenyl-pyrazol-4-yl)methyl]benzene (14a):



mp 110-113°C; IR: 1789 ($CH_3\underline{C}=O$); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.81 (s, 12H, CH_3), 2.05 (s, 12H, $COCH_3$), 5.14 (s, 2H, CH), 7.22-7.42 (m, 24H, aryl-CH); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 13.91 (C^6), 20.40 (C^{17}), 36.49 (C^{12}), 108.53 (C^4), 123.25 (C^8), 127.61 (C^{14}), 127.76 (C^{10}), 128.71 (C^{16}), 129.52 (C^{15}), 129.69 (C^9), 138.46 (C^7), 141.05 (C^{13}), 142.36 (C^3), 148.75 (C^5), 167.49 (C^{11}). MS: Calcd. for $C_{56}H_{50}N_8O_8$, 963.06. Found (FAB): $^m/_z$ = 964 (M^+), 922 (M^+ - H_2C=C=O), 880 (M^+ - 2 H_2C=C=O), 620 (M^+ - 4 H_2C=C=O - 1 pyrazole).

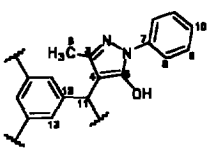
Bis-1,4-[di-(3-methyl-5-methylcarbonyloxy-1-phenyl-pyrazol-4-yl)methyl]benzene (14b):



mp 290-292°C; IR: 1787 ($CH_3\underline{C}=O$); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.84 (s, 12H, CH_3), 2.03 (s, 12H, $COCH_3$), 5.13 (s, 2H, CH), 7.27-7.31 (m, 20H, aryl CH), 7.43 (s, 4H, terephthal-CH); ^{13}C NMR (200 MHz, $CDCl_3$) δ: 13.98 (C^6), 20.38 (C^{15}), 36.36 (C^{12}), 108.52 (C^4), 123.34 (C^8), 127.81 (C^{10}), 129.38 (C^{14}), 129.69 (C^9), 138.42 (C^7), 139.25 (C^{13}), 142.35 (C^3), 148.67 (C^5), 167.48 (C^{11}). MS: Calcd. for $C_{56}H_{50}N_8O_8$,

963.06. Found (FAB): $^{m}/_{z}$ = 964 (M^+), 922 (M^+ - $H_2C{=}C{=}O$), 880 (M^+ - 2 $H_2C{=}C{=}O$), 620 (M^+ - 4 $H_2C{=}C{=}O$ - 1 pyrazole).

Tris-1,3,5-[di-(5-hydroxy-3-methyl-1-phenyl-pyrazol-4-yl)methyl]benzene (15):



mp 210-213°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ: 2.18 (s, 18H, CH_3), 4.75 (s, 3H, CH) 7.15 (s, 3H, aryl), 7.24 (dd, 6H, phenyl-p-CH), 7.38 (dd, 12H, phenyl-m-CH), 7.63 (d, 12H, phenyl-o-CH), 14.19 (s, OH); ^{13}C NMR (200 MHz, DMSO-d_6) δ: 11.80 (C^6), 34.06 (C^{11}), 104.90 (C^4), 121.17 (C^8), 123.93 (C^{13}), 125.78 (C^{10}), 129.03 (C^9), 137.64 (C^7), 143.14 (C^{12}), 146.55 (C^3), 157.70 (C^5). MS: Calcd. for $C_{69}H_{60}N_{12}O_6$, 1153.32. Found (FAB): $^{m}/_{z}$ = 1154 (M^+), 979 (M^+ - 1 pyrazole), 805 (M^+ - 2 pyrazole), 632 (M^+ - 3 pyrazole).

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References

1. Atwood, J. L.; Davies, J. E. D. (Eds.) *Inclusion Compounds*, Academic Press, London, Vol. 1-3, 1984, Vol. 4, 1991
2. Weber, E. *Top. Curr. Chem.* **1987**, *140*, 1-20
3. (a) Wright, J. D. *Molecular Crystals*, Cambridge University Press, Cambridge, 1987
   (b) Desiraju, Y. D. *Crystal Engineering: The Design of Organic Solids*, Material Science Monographs, Elsevier, Amsterdam, 1989
4. (a) Goldberg, I.; Stein, Z.; Kai, A.; Toda, F. *Chem. Lett.* **1987**, 1617-1620
   (b) Goldberg, I.; Stein, Z.; Tanaka, K.; Toda, F. *J. Incl. Phenom.* **1988**, *6*, 15-30
   (c) Goldberg, I.; Stein, Z.; Tanaka, K.; Toda, F. *J. Incl. Phenom. Mol. Recogn. Chem.* **1991**, *10*, 97-107
5. (a) Suzuki, H. *Tetrahedron Lett.* **1992**, *33*, 6319-6322
   (b) Suzuki, H.; Tagaki, H. *Tetrahedron Lett.* **1993**, *34*, 4805-4806
6. Desimoni, G.; Gamba, A.; Righetti, P.; Tacconi, G. *Gazz. Chim. Ital.* **1972**, *102*, 491-506
7. (a) F. Strohbusch; Bratan-Meyer, S.; Hänsel, W. *Z. Naturforsch.* **1976**, *316*, 1106-1115
   (b) Drück, U.; Littke, W. *Acta Cryst.* **1980**, *B36*, 3002-3007
8. Bechtel, F.; Gaultier, J.; Hauw, C. *Cryst. Struct. Comm.* **1973**, *2*, 469-472
9. Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd Edition, VCH Verlag, Weinheim, 1989, p. 287
10. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120-126

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