Guest-Host Systems of 1,3,5-Tristyrylbenzenes

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Z. Naturforsch. **58b,** 775 – 781 (2003); received April 2, 2003

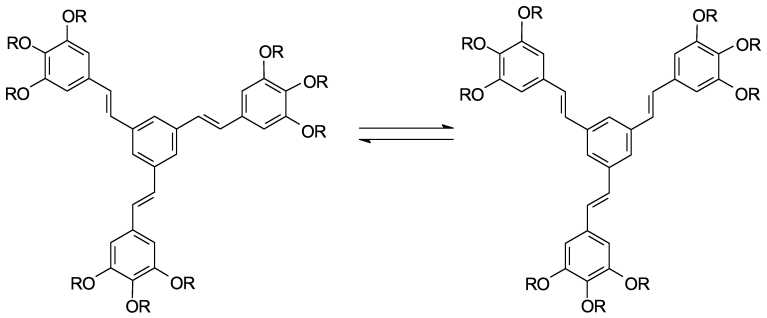
(*E*,*E*,*E*)-1,3,5-Tris(3,4,5-trimethoxystyryl)benzene (**1a**) forms monoclinic crystals of the space group $P2_1/c$. Incorporation of three transoid diacetyl guest molecules between the three arms leads to triclinic crystals of the space group $P1$. The styryl groups, originally present in a non-symmetrical conformation, are simultaneously transformed to a C_3 arrangement. (*E*,*E*,*E*)-1,3,5-Tris-(3,4,5-tripropoxystyryl)benzene (**1b**) forms monoclinic crystals of the space group $P2_1/c$. The C_3 arrangement of the styryl groups is present in the first, the unsymmetrical arrangement in the second modification. Incorporation of two acetone guests in the largest and the middle-sized angle space between the styryl arms in the unsymmetrical arrangement, leads to monoclinic crystals of the space group $P2_1/n$. The third (smallest) angle space is filled with a propoxy chain of the neighboring molecule. The pure host crystals show significant deviations from planarity which are strongly reduced by the incorporation of the guest molecules.

Key words: Guest-Host Crystals, Triplet Sensitizer

Introduction

Stilbenoid dendrimers [1 – 5] combine interesting photochemical and photophysical properties of stilbenes [6] with the particular character of dendrimers with relatively rigid arms. Such dendrons are not capable of a backfolding; therefore the molecular density increases from the core to the periphery of the systems. Consequently cavities must exist close to the core, a feature which could be nicely visualised by molecular models calculated with the CERIUS 2.0 software [4]. These cavities are large enough to host guest molecules. Toluene for example is so firmly included in the higher stilbenoid dendrimers that it flies in the vacuum together with the molecular ions $M^{+\bullet}$ in the MALDI-TOF mass spectroscopy [4].

We are particularly interested in *optical switching* processes of liquid crystals which are formed by



conformer **A** conformer **B**

1	a	b	c	d
R	CH_3	*n*-C_3H_7	*n*-C_6H_{13}	*n*-$C_{12}H_{25}$

Scheme 1.

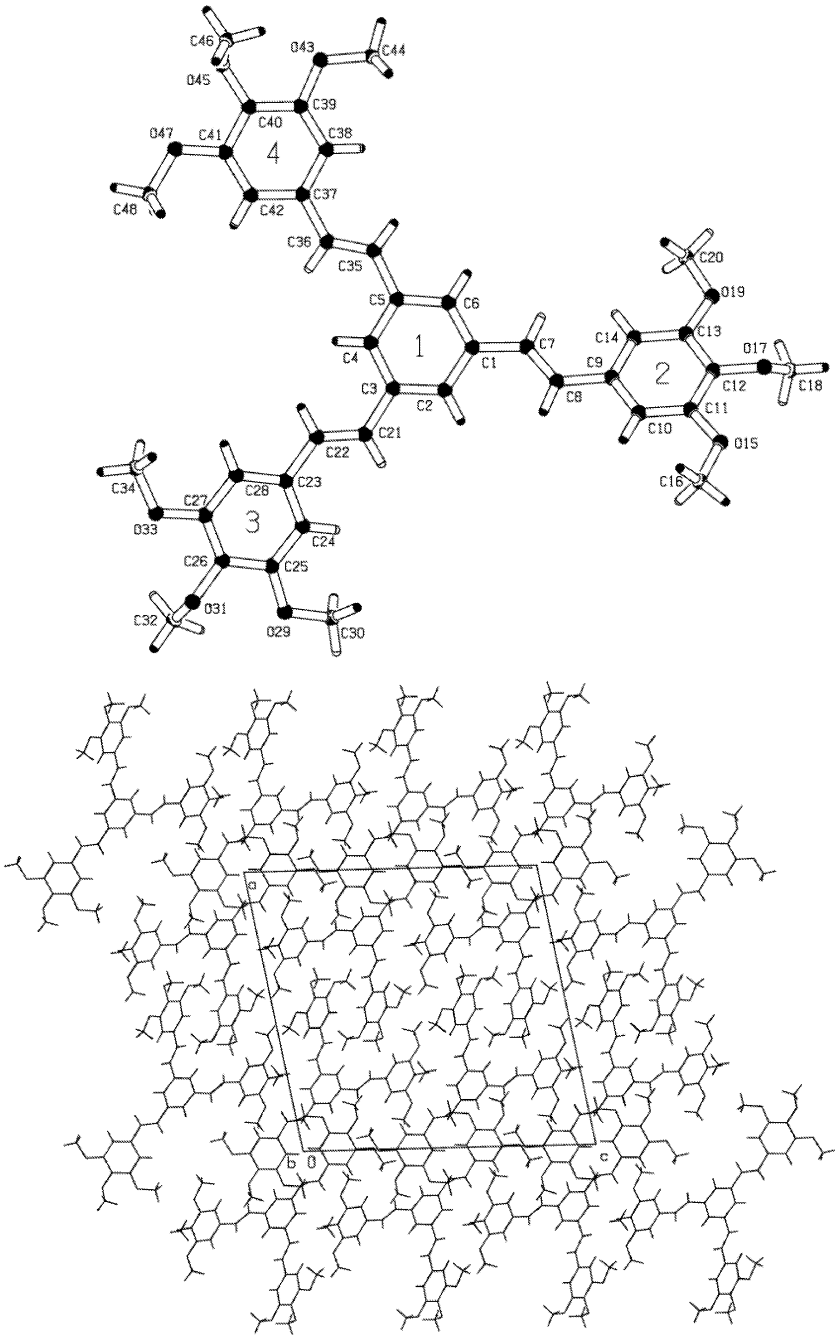


Fig. 1. a) PLATON plot at the crystal structure of (*E*,*E*,*E*)-1,3,5-tris(3,4,5-trimethoxy-styryl)benzene (**1a**) measured at 22 °C (upper part); b) packing of the crystals viewed along the *b* axis (lower part).

stilbenoid dendrimers. The parent compound, which may be assigned to the lowest generation of stilbenoid dendrimers, is represented here by (*E*,*E*,*E*)-1,3,5-tristyrylbenzenes **1a – d** with alkoxy sidechains [2,4,5]. The molecules can exist in two conformational arrangements; the statistical ratio **A** : **B** would be 1 : 3.

Triplet sensitizers provoke in solution an efficient photochemical *trans/cis* isomerization of **1a – d** without the backdraw of an irreversible CC bond formation.

The cavities in the liquid crystalline phases of **1c,d** can be filled with triplet sensitizers as guest molecules. Now the point of question was whether the smaller

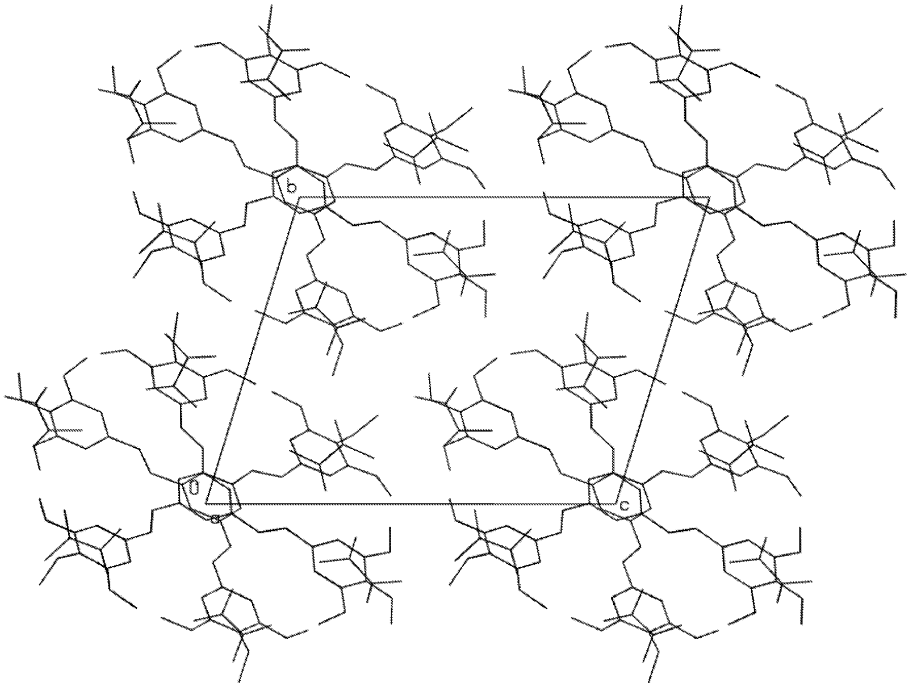


Fig. 2. PLATON plots of the guest-host system **1a'** measured at −153 °C; a) symmetrical arrangement of the diacetyl guests (upper part); b) asymmetrical arrangement of the diacetyl guests; c) packing of the crystals viewed along the *c* axis (lower part).

systems **1a,b** which form crystalline states can be also doped with triplet sensitizers like acetone or 2,3-butanedione (diacetyl).

Results and Discussion

Crystallization of **1a** from diethyl ether yielded monoclinic crystals of the pure host; crystallization from diacetyl however, gave triclinic crystals with three guest molecules of diacetyl per host molecule. Crystallization of **1b** from acetone led to monoclinic crystals with two guest molecules of acetone per host molecule. It turned out that the third cavity (angle space between the arms) remains occupied by the propoxy sidechain of a neighbor molecule. Crystallization of **1b** from diacetyl yielded monoclinic crystals of the pure host.

The crystal structure of **1a** is shown in Fig. 1. The conformational arrangement of the three styryl groups corresponds to type **B**. Hence, the angle spaces between the styryl groups have different sizes. They are filled with the sidechains of neighboring molecules.

When the crystallization of **1a** was performed in diacetyl instead of diethyl ether, guest-host crystals **1a'** were obtained. Actually, two in their geometry slightly differing host molecules were found, both having the C_3 arrangement **A**. The guest molecules occupy the angle areas – one *transoid* diacetyl per area. Their arrangement corresponds also to C_3 in the first type of host molecules, but not in the second (Figs. 2a and 2b). Neighboring host molecules have their central benzene rings in almost parallel planes but their arms are turned by approximately 60° against each other. Thus, a pair of neighboring tristyrylbenzene molecules **1a** has almost a center of symmetry. Consequently, the three diacetyl guests in the angle areas of the host molecule interact with the outer benzene rings of the neighboring host molecule (Fig. 2c).

The crystal structure of **1b** at −73 °C is shown in Fig. 3a. In contrast to **1a**, the pure compound **1b** has a conformational C_3 arrangement **A**. The monoclinic space group $P2_1/n$ present at −73 °C is transformed at lower temperatures to a somewhat closer packing in the monoclinic space group $P2_1/c$ (Fig. 3b). The DSC measurement reveals in the first as well as in the second heating curve a phase transition with an onset temperature of −73.2 °C ($\Delta H = -7\ J \cdot g^{-1}$); the cooling curve shows at the same rate (10 degrees per minute) a broad transition with a peak maximum at 88.5 °C (undercooling effect). The molecular process, which is responsible for the transformation, corresponds to the conformational change **A** ⇄ **B**, where **B** is preferred at low temperatures. Such a second order phase transition could not be found for **1a**.

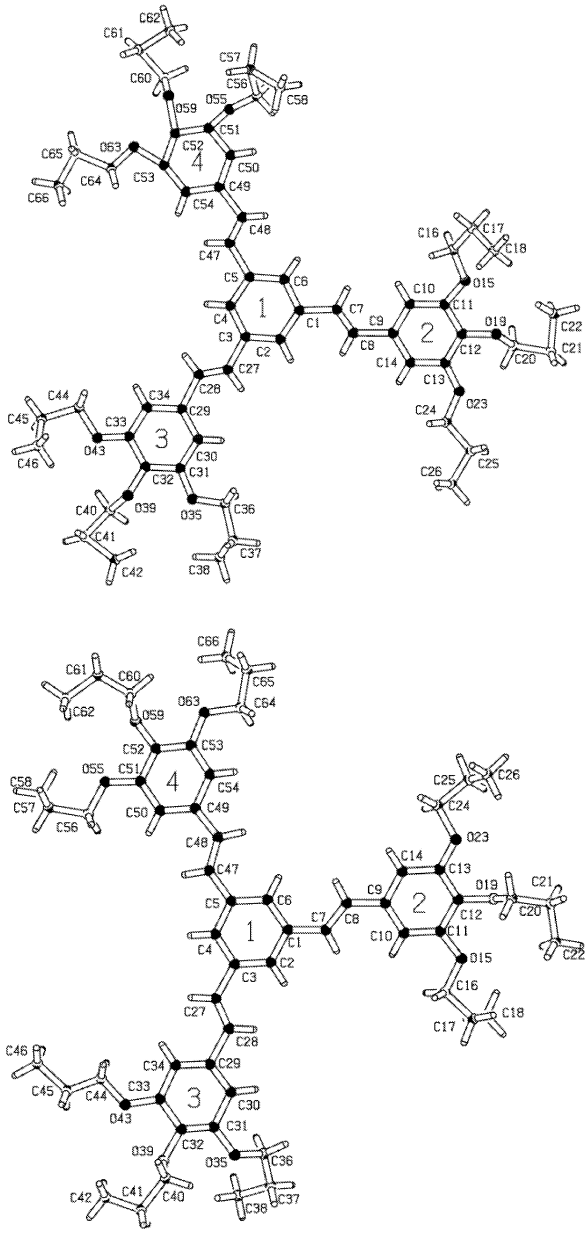


Fig. 3. PLATON plot of the crystal structure of (E,E,E)-1,3,5-tris(3,4,5-tripropoxystyryl)-benzene a) **1b** measured at −73 °C (upper part); b) **1b** measured at −153 °C (lower part).

Crystallization of **1b** from acetone leads to a guest-host crystal **1b'**. The conformation of the host molecules corresponds to **B** with three different angle spaces. The bigest one and the mean are occupied by acetone guests, the smallest by the propoxy chain of a neighboring molecule (Fig. 4).

Table 1. Angles (degrees) between the benzene ring planes 1,2,3 and 4 in the crystals of **1a**, **1a'**, **1b** and **1b'**.

Compound	Figure	Plane	Plane 2	Plane 3	Plane 4
1a	1a	1	29.9	20.2	7.8
		2		46.0	35.4
		3			12.4
1a'	2a	1	2.4	5.7	8.5
molecule A		2		7.9	10.9
		3			4.4
molecule B	2b	1	0.6	7.6	7.4
		2		8.2	7.9
		3			1.1
1b	3a	1	10.8	13.8	16.6
molecule A		2		24.0	9.0
		3			26.6
molecule B	3b	1	16.6	10.7	15.3
		2		11.0	28.6
		3			25.9
1b'	4a	1	0.7	5.2	6.7
		2		8.5	6.1
		3			7.3

The bond lengths and bond angles of **1a** and **1b** as well as of the guest-host systems **1a'** and **1b'** are all within the normal range. Special attention has to be directed to the planarity of the stilbenoid compounds. Of course, conjugation favors the planarity; however, the increase in potential energy caused by torsions around the single bonds of the styryl groups is small [6]. Table 1 summarizes the angles between the benzene rings 1,2,3 and 4 of the structures shown in Figs. 1a, 2a, 3a, 3b and 4b. There are significant deviations from planarity in the host compounds **1a** and **1b**. Incorporation of the guest molecules (**1a**, **1b** → **1a'**, **1b'**) provokes a drastic decrease of each angle θ; that means the guest ketones planarize the stilbenoid host molecules. The most striking example concerns the ring planes 2 and 3 in **1a**; the angle θ = 46.0° for the pure host decreases in the guest-host crystals **1a'** to 7.9° and 8.2°, respectively (Table 1).

Conclusion

1,3,5-Tristyrylbenzenes (**1a – d**) represent the lowest generation of stilbenoid dendrimers. Optical switching processes of these compounds are based on *cis/trans* isomerization processes which are in the triplet state T_1 undisturbed by CC bond formations. It could be shown here that three transoid diacetyl molecules can be included in the crystals of the methoxy compound **1a**. The crystals of the corresponding compound **1b** with nine propoxy chains can host two guest molecules of acetone. The third an-

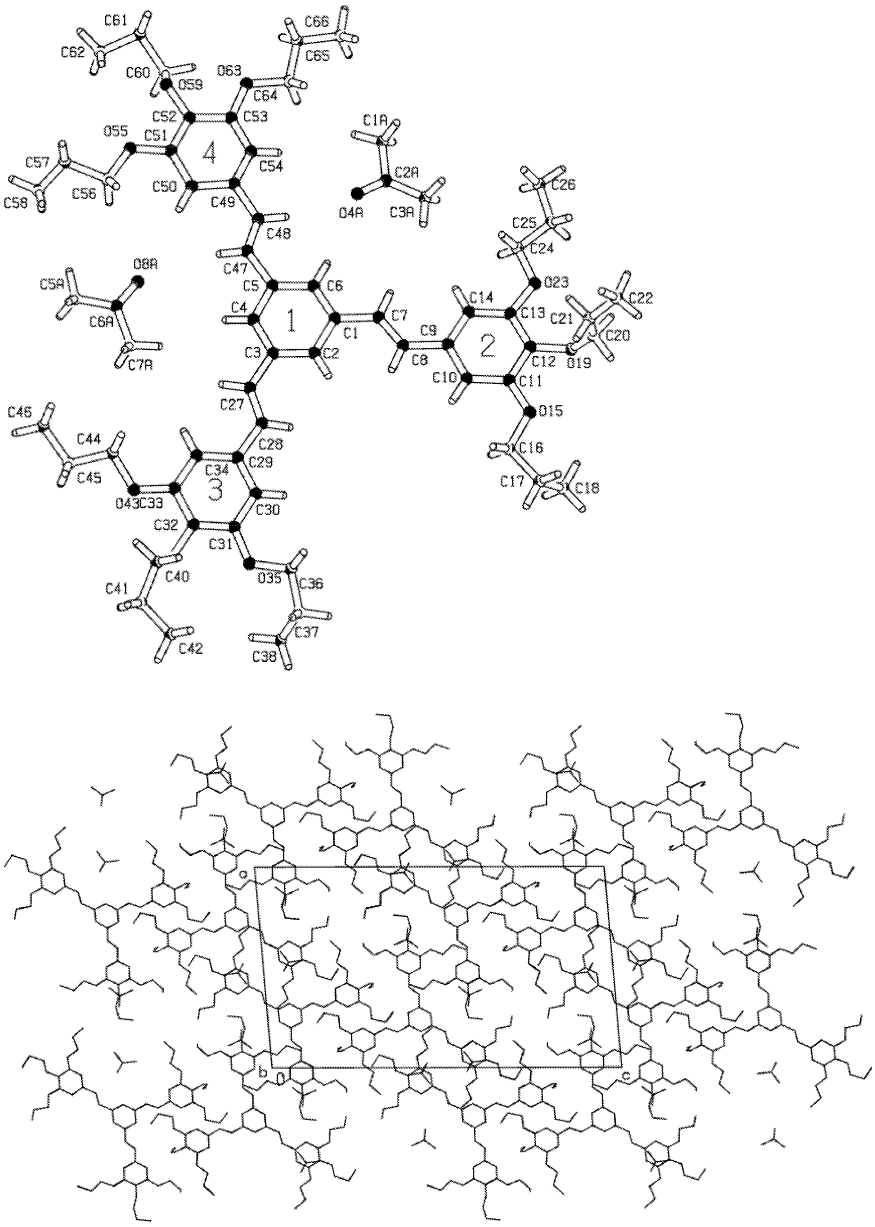


Fig. 4. PLATON plot of the guest-host system **1b'** measured at −153 °C (upper part); b) packing of the crystals viewed along the *b* axis (lower part).

gle space (between the trialkoxystyryl groups) is occupied by the propoxy chain of a neighboring molecule of **1b**. The major effect, caused by the inclusion of the guest molecules, corresponds to conformational changes (**1a** → **1a'**) and to a far-reaching planarization of the guest molecules (**1a** → **1a'**, **1b** →**1b'**). One can assume that the incorporation of guest molecules in the LC phases of **1c** and **1d** is realized on a similar design.

Experimental Section

Synthesis

Compounds **1a** and **1b** were prepared according to the literature [4].

Crystal structure determinations

Crystal data and full details of the data collection and data processing are listed in Table 2. The following computer software was used: Data collection: Enraf-Nonius Software

Table 2. Details of the X-ray crystal structure analysis of the compounds **1a**, **1a'**, **1b**, **1b'**.

Compound	**1a**	**1a'**	**1b**	**1b**	**1b'**
Formula	$C_{39}H_{42}O_9$	$C_{39}H_{42}O_9 \cdot 3\ C_4H_6O_2$	$C_{57}H_{78}O_9$	$C_{57}H_{78}O_9$	$C_{57}H_{78}O_9{\cdot}2C_3H_6O$
M_r	654.7	912.99	907.20	907.20	1023.35
Habit	colorless block	yellow needle	yellow dicks	yellow dicks	colorless block
Crystal size (mm)	$0.04 \times 0.56 \times 0.59$	$0.08 \times 0.20 \times 0.50$	$0.195 \times 0.335 \times 0.410$	$0.195 \times 0.335 \times 0.410$	$0.26 \times 0.45 \times 0.83$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
Cell constants:					
a (Å)	21.889(3)	9.7680(5)	12.570	12.9750(10)	20.9341(13)
b (Å)	7.4099(14)	14.1803(10)	37.437	36.0946(10)	8.1221(6)
c (Å)	22.483(4)	18.0875(10)	12.973	22.3778(10)	36.294(2)
α(°)		72.9031(10)			
β(°)	100.594(8)	87.1362(10)	118.30	93.325(3)	94.844(6)
γ(°)		86.4462(10)			
V (Å^3)	3584.4(10)	2387.5(2)	5375(1)	10462(2)	6149.0
Z	4	2	4	8	4
D_x (Mg m^{-3})	1.213	1.270	1.121	1.152	1.105
Radiation	Cu-K$_\alpha$	Mo-K$_\alpha$	Mo-K$_\alpha$	Mo-K$_\alpha$	Cu-K$_\alpha$
μ (mm^{-1})	0.7	0.09	0.07	0.08	0.59
F(000)	1392	972	1968	3936	2224
T (K)	295	120	200	120	298
θ_{max} (°)	73.8	27.5	25.5	27.5	75.0
No. of refl.:					
measured	8061	25033	9790	67945	12632
indep.	7256	15937	9645	22956	12632
observed	4470	10788	3957	8675	4183
$[F_0/\sigma(F_0) > 4.0]$					
R_{int}	0.0346	0.1123	0.0719	0.1434	0.0713
Parameters	433	1189	217	1057	668
Restraints	0	25	23	15	15
$wR(F^2$, all refl.)	0.2362	0.2717	0.8487	0.5881	0.4051
$R(F^2, > 2\sigma(F^2))$	0.0763	0.0894	0.3734	0.2410	0.1069
S	1.026	1.106	0.916	1.682	1.022
max. $\Delta\rho$ (e Å^3)	0.79	1.04	0.52	2.72	0.58
min. $\Delta\rho$ (e Å^3)	−0.38	−0.60	−0.89	−0.83	−0.21

V 5 (**1a**) and Collect (Nonius BV, 1997 – 2000) (**1a'**, **1b**, **1b'**. Data reduction: Corinc [7] for **1a** and Denzo [8] for all other structures. The structures were solved with SIR-92 [9] (**1a'** with DIRDIF) [10] and refined by full-matrix least squares techniques on F^2 with SHELXL-97 [11]. For all structures H atoms were placed at calculated positions and refined with riding motion. The crystals of compound **1b** could be obtained with poor quality only and diffracted very weakly. The structure at 200 K was treated with an isotropic refinement. At 120 K anisotropic refinement for most non-H atoms was possible. The figures 1a, 2a, 2b, 3a, 3b and 4a correspond to PLATON plots [12].

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 206997 – 207001. Copies of the data can be obtained free of charge on application to: The Director. CCDC, 12 Union Road, Cambridge CB2 5U, UK.

Acknowledgements

We wish to acknowledge the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their financial support.

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