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Structure and Conformation of Substituted Cycloheptatrienes.
II. 2,3,4,5-Tetraphenyl-1,3,5-cycloheptatriene*

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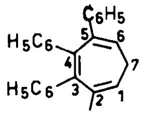
Abstract

$C_{31}H_{24}$ is monoclinic, space group $P2_1/a$, with $a = 32{\cdot}46\,(3)$, $b = 7{\cdot}885\,(5)$, $c = 8{\cdot}78\,(1)$ Å, $\beta = 92{\cdot}30\,(1)°$, $Z = 4$. The structure was refined to $R = 0{\cdot}056$ for 1361 counter reflections. The ring is boat-shaped with structure angles $\alpha = 50{\cdot}7$, $\beta = 36{\cdot}9°$. Empirical force-field calculations predict $\alpha = 48{\cdot}8$, $\beta = 19{\cdot}9°$ for the isolated molecule and $\alpha = 52{\cdot}0$, $\beta = 35{\cdot}9°$ with the inclusion of packing effects. The sublimation enthalpy is predicted to be 187 kJ mol^{-1}. The enthalpy of the inversion barrier between the two boat forms has been calculated to be 64 kJ mol^{-1}.

Introduction

This work forms part of a sequence of structure investigations (part I: Stegemann & Lindner, 1979) on substituted cycloheptatrienes. While the flexibility of the cycloheptatriene moiety has been investigated in detail by NMR spectroscopy (for a review see Tochtermann, 1970) only one X-ray analysis of a substituted cycloheptatriene (Davis & Tulinsky, 1966) has been reported.

We found it necessary to analyse more crystal structures in our attempt to clarify the substituent-dependence on the conformation of the cycloheptatriene moiety. Additionally, empirical force-field calculations have been found to be a versatile tool for rationalizing the X-ray structure results. Differences from the predicted structures of the isolated molecules can be explained by inclusion of packing effects in the calculations. While the general discussion on all observed effects will be included in the last part of the series, here we report the structure of 2,3,4,5-tetraphenyl-1,3,5-cycloheptatriene (I).



(I)

Table 1. *Crystal data*

$C_{31}H_{24}$, $M_r = 396$, space group $P2_1/a$

$a = 32{\cdot}46\,(3)$ Å	$V = 2245{\cdot}4$ Å^3
$b = 7{\cdot}885\,(5)$	$Z = 4$
$c = 8{\cdot}78\,(1)$	$\rho_o = 1{\cdot}17$ Mg m^{-3} (flotation)
$\beta = 92{\cdot}30\,(1)°$	$\rho_c = 1{\cdot}17$
	$\mu = 0{\cdot}43$ mm^{-1}

Experimental

Crystals were grown from C_2H_5OH by slow evaporation as transparent plates developed on [001] (Kessler & Bicker, 1976). Systematic absences ($h0l$: $h = 2n$, $0k0$: $k = 2n$) were those characteristic of $P2_1/a$. Crystal data are given in Table 1. Intensities for 3424 independent reflections were collected on a two-circle diffractometer up to $\theta = 55°$ ($h0l$ to $h5l$) in the ω–2θ scan mode with Cu $K\alpha$ graphite-monochromatized radiation. The data were corrected for background and geometrical factors, but not for absorption. 1361 reflections with $|E| > 4\sigma_E$ were used in the final refinement.

Structure determination and refinement

The structure was solved by direct methods (*SHELX*77, Sheldrick, 1977). Scattering factors were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); for H the form factors of a terminal H atom were used (Stewart, Davidson & Simpson, 1965). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms

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* This work forms part of the thesis of Jürgen Stegemann.

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Table 2. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and their e.s.d.'s*

	x	y	z	$U_{eq.}$ (Å^2)*
C(1)	3487 (2)	4925 (9)	7046 (6)	0·060
C(2)	3743 (2)	3685 (8)	6660 (5)	0·054
C(3)	3811 (1)	2157 (7)	7580 (5)	0·051
C(4)	3498 (2)	1336 (6)	8260 (5)	0·049
C(5)	3057 (1)	1789 (7)	7974 (5)	0·058
C(6)	2928 (2)	3363 (9)	8000 (7)	0·083
C(7)	3206 (2)	4836 (10)	8392 (7)	0·060
C(21)	4006 (2)	3965 (8)	5329 (6)	0·058
C(22)	3990 (2)	2797 (9)	4113 (7)	0·074
C(23)	4233 (2)	3007 (10)	2869 (7)	0·083
C(24)	4510 (2)	4293 (10)	2856 (8)	0·088
C(25)	4539 (2)	5447 (10)	4042 (8)	0·084
C(26)	4287 (2)	5257 (9)	5276 (7)	0·066
C(31)	4250 (2)	1622 (8)	7769 (7)	0·061
C(32)	4430 (2)	462 (9)	6884 (7)	0·077
C(33)	4845 (2)	−3 (11)	7068 (8)	0·094
C(34)	5088 (3)	958 (12)	8156 (9)	0·101
C(35)	4922 (2)	2078 (11)	9035 (8)	0·082
C(36)	4504 (2)	2552 (9)	8831 (7)	0·069
C(41)	3567 (2)	−86 (8)	9416 (6)	0·049
C(42)	3822 (2)	−1434 (10)	9243 (8)	0·066
C(43)	3886 (2)	−2636 (11)	10444 (9)	0·084
C(44)	3688 (2)	−2434 (11)	11802 (9)	0·073
C(45)	3428 (2)	−1147 (13)	11922 (8)	0·074
C(46)	3353 (2)	88 (10)	10759 (8)	0·072
C(51)	2773 (2)	319 (7)	7489 (6)	0·052
C(52)	2371 (2)	311 (9)	7940 (7)	0·064
C(53)	2099 (2)	−923 (11)	7368 (8)	0·074
C(54)	2224 (2)	−2082 (11)	6356 (8)	0·073
C(55)	2622 (2)	−2136 (10)	5930 (8)	0·065
C(56)	2895 (2)	−864 (9)	6507 (7)	0·064
H(C1)	341 (1)	607 (6)	643 (4)	0·05
H(C6)	269 (1)	367 (5)	785 (4)	0·01
H(C7)	305 (3)	626 (13)	862 (9)	0·28
H′(C7)	339 (2)	443 (6)	927 (6)	0·07
H(C22)	379 (1)	215 (6)	422 (6)	0·07
H(C23)	419 (2)	207 (7)	193 (6)	0·12
H(C24)	473 (1)	443 (6)	208 (5)	0·06
H(C25)	478 (2)	651 (8)	405 (6)	0·13
H(C26)	435 (1)	619 (6)	614 (5)	0·05
H(C32)	426 (1)	−28 (6)	624 (5)	0·06
H(C33)	497 (2)	−104 (9)	637 (6)	0·11
H(C34)	538 (2)	81 (7)	823 (6)	0·10
H(C35)	505 (3)	341 (12)	963 (9)	0·21
H(C36)	437 (1)	347 (5)	941 (4)	0·02
H(C42)	401 (2)	−156 (7)	816 (6)	0·08
H(C43)	411 (2)	−349 (9)	1022 (7)	0·13
H(C44)	366 (3)	−323 (11)	1290 (9)	0·20
H(C45)	329 (2)	−57 (6)	1276 (6)	0·08
H(C46)	311 (2)	49 (10)	1087 (8)	0·15
H(C52)	227 (2)	112 (7)	871 (6)	0·09
H(C53)	184 (2)	−70 (6)	776 (5)	0·06
H(C54)	202 (1)	−322 (7)	603 (5)	0·08
H(C55)	274 (1)	−262 (6)	518 (5)	0·05
H(C56)	315 (2)	−67 (8)	605 (6)	0·10

* Calculated by $U_{eq.} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$ for C atoms and $U_{eq.} = U$ for H atoms.

reduced R to 0·132. A difference map at this stage revealed the positions of all 24 H atoms. Further cycles with isotropic H atoms gave the final R of 0·056 with average shifts in heavy-atom parameters $<\frac{1}{3}$ of the e.s.d.'s. Atomic coordinates are presented in Table 2.*

Results

Fig. 1 is a sketch of the molecule (Motherwell, 1975) showing the numbering and all non-hydrogen bond distances. Fig. 2 shows the bond angles and some selected dihedral angles. Least-squares planes and angles of the molecule are collected in Table 3.

The heptatriene ring displays alternating bond lengths and equalized bond angles (122–124°) with the exception of the angle at the sp^3 C atom which is diminished by 6° compared to the normal valence

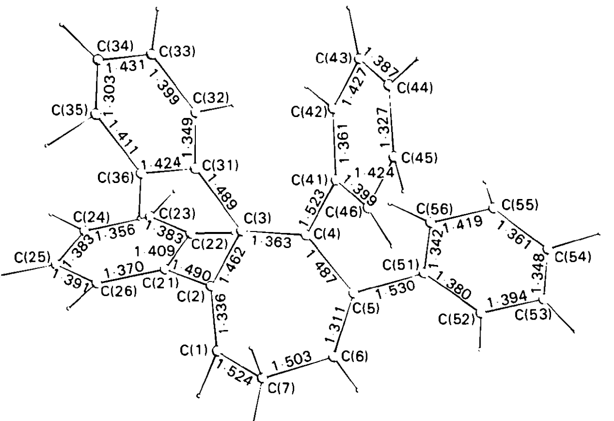

Fig. 1. Bond lengths (Å) of 2,3,4,5-tetraphenyl-1,3,5-cycloheptatriene ($\sigma_{CC} = 0·003$ Å).

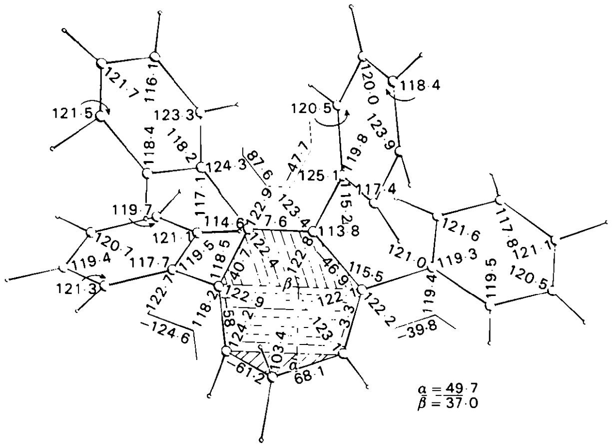

Fig. 2. Bond angles and some dihedral angles (°) ($\sigma_{CCC} = 0·2°$; $\sigma_{CCCC} = 0·4°$).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35414 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

angle. The boat-shaped structure shows no C_s symmetry: in particular the surrounding of the tip is asymmetric. The twisting of the double bonds (3–8°) and the out-of-plane deformation angles at the sp^2 C atoms (2–7°) display the internal strain due to the bulky phenyl groups which are not in conjugation with the double bonds of the heptatriene moiety. The rotation angles vary from 41 to 82°.

Packing

The crystal packing is determined in two dimensions by the formation of translational chains of molecules along **b** and **c**. These cell constants correspond to the dimensions of a single molecule. Shortest intermolecular distances within these translational layers are in the **b** direction C(7)···C(43) 3·43 and C(7)···C(55) 3·69 Å and in the **c** direction C(23)···C(36) 3·70 Å (Table 4). In the **a** direction are stacked four of these layers interrelated by the screw axes and the inversion centres. The molecules on one layer are placed within the holes formed by the neighbouring layers and firmly held together by the phenyl rings (Fig. 3). The shortest intermolecular distance is C(25)···C(25) 3·45 Å between the molecules *x*,*y*,*z* and 1 − *x*, 1 − *y*, 1 − *z*.

The next layers in the **a** direction are formed by the inverted screw axis with no contact to the first layer and by the screw axis (Fig. 4). The shortest distance here is between C(7) of molecule *x*,*y*,*z* and C(52) of molecule 1 − *x*, −*y*, 1 − *z* (3·81 Å).

Table 3. *Least-squares planes, with maximum deviations* (Å) *out of the planes* (*e.s.d.* = 0·01 Å), *and structure angles* (°) (*e.s.d.* = 0·1 °)

(I)	C(6)–C(7)–C(1)		
(II)	C(1)–C(2)–C(5)–C(6)	0·03	C(6)
(III)	C(2)–C(3)–C(4)–C(5)	0·03	C(3)
(IV)	C(21)–C(22)–C(23)–C(24)–C(25)–C(26)	0·02	C(22)
(V)	C(31)–C(32)–C(33)–C(34)–C(35)–C(36)	0·03	C(35)
(VI)	C(41)–C(42)–C(43)–C(44)–C(45)–C(46)	0·02	C(44)
(VII)	C(51)–C(52)–C(53)–C(54)–C(55)–C(56)	0·02	C(54)

Rotation angles

Phenyl (IV)/*P*[C(1),C(2),C(3)]	62·0	IV/II	49·7
Phenyl (V)/*P*[C(2),C(3),C(4)]	98·2	V/II	61·3
Phenyl (VI)/*P*[C(3),C(4),C(5)]	47·9	VI/II	46·8
Phenyl (VII)/*P*[C(4),C(5),C(6)]	41·0	VII/II	41·9

IV/V 56·7, V/VI 72·8, VI/VII 82·8, IV/VII 31·6

Out-of-plane deformation angles at the sp^2 C atoms of the heptatriene ring

C(2) 6·8, C(3) 2·7, C(4) 1·8, C(5) 6·0

Structure angles

Structure analysis:	α = I/II = 50·7, β = III/II = 36·9
Isolated-molecule calculation:	α = I/II = 48·8, β = III/II = 19·9
Packed-molecule calculation:	α = I/II = 52·0, β = III/II = 35·9

Table 4. *Shortest intra- and intermolecular distances* (Å) (*e.s.d.* = 0·01 Å)

The values in parentheses are those for the equivalent H···H [or H···C for C(51)] distances.

		Symmetry operation
C(1)···C(6)	2·37	
C(44)···C(25)	3·72 (3·29)	(*x*, −1 + *y*, 1 + *z*)
C(7)···C(43)	3·43 [2·95, H′(C7)]	(*x*, 1 + *y*, *z*)
C(7)···C(55)	3·69 [3·27, H(C7)]	
C(26)···C(33)	4·42 (2·97)	
C(36)···C(43)	4·54 (2·65)	
C(23)···C(36)	3·70 (2·56)	(*x*, *y*, −1 + *z*)
C(22)···C(45)	4·05 (2·94)	
C(56)···C(45)	4·45 (2·95)	
C(25)···C(25)	3·45 (3·22)	(1 − *x*, 1 − *y*, 1 − *z*)
C(25)···C(34)	3·66 (2·94)	
C(33)···C(23)	3·81 (3·17)	(1 − *x*, −*y*, 1 − *z*)
C(33)···C(32)	4·29 (3·61)	
C(34)···C(36)	4·02 (4·02)	(1 − *x*, −*y*, 2 − *z*)
C(34)···C(42)	3·74 (2·98)	
C(22)···C(53)	3·85 (3·13)	(0·5 − *x*, 0·5 + *y*, 1 − *z*)
C(6)···C(55)	3·84 (3·13)	
C(51)···C(55)	3·79 (3·26)	
C(52)···C(45)	3·82 (3·40)	(0·5 − *x*, 0·5 + *y*, 2 − *z*)
C(6)···C(46)	4·55 (3·21)	
C(7)···C(52)	3·81 [3·12, H′(C7)]	

Discussion

The conformation of the phenyl groups should be very sensitive to the molecular stacking. In fact Fig. 4 shows that the rings interpose each other. These effects are not taken into account if one tries to predict the molecular geometry by calculations on the isolated molecule. Fig. 5 shows the result of an empirical force-field calculation with the program *MCA* (molecular conformation analysis; Huler & Warshel, 1974) with modified and extended parameters for force-field and π-SCF calculation (Stegemann, 1979).

All phenyl groups are rotated into nearly parallel orientations vertical to the heptatriene ring system. The structure angle β decreases significantly from 37 to 20°. In comparison with the results obtained by other programs (*e.g.* *PIMM*; π-SCF-MO molecular mechanics program; Lindner, 1974) one sees that this geometry is quite normal and not an artefact of our procedure; nevertheless, the calculated structure of the isolated molecule is insufficient to explain the experimental results. A calculation performed with the *MCA* program which takes into account the packing effects revealed that with the isolated-molecule structure no close-packing pattern can be achieved (sublimation enthalpy >0 kJ mol^{-1}). From the table of shortest intermolecular distances found in the crystal packing one can see the interrelations between the phenyl rings at C(2) and C(3) and between those at C(4) and C(5). Neighbouring rings are interposed in such a way that

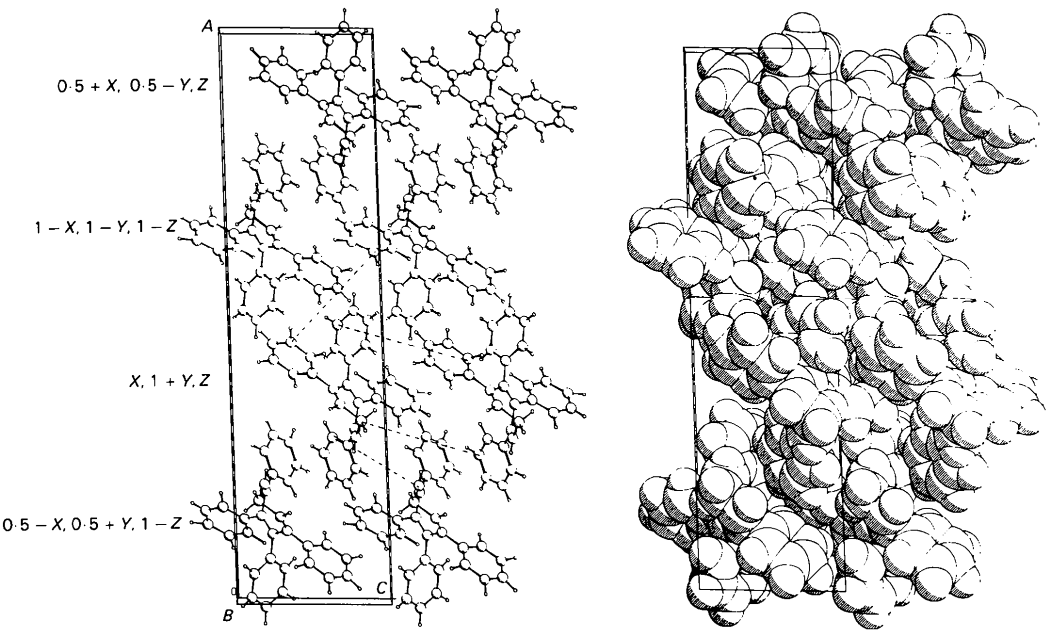

Fig. 3. A view down **b** with **c** horizontal and **a** vertical. Left: ball-and-stick model; right: van der Waals representation; the unit cell is outlined.

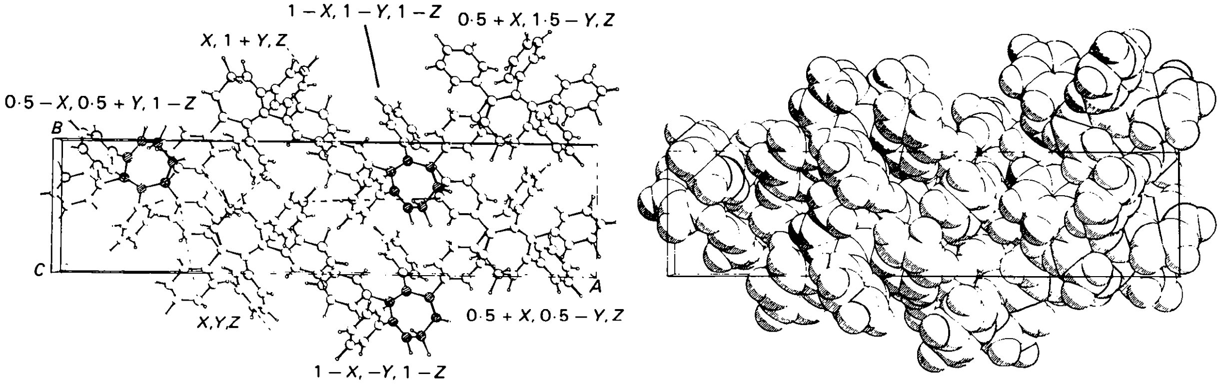

Fig. 4. A view down **c** with **a** horizontal and **b** vertical. Left: ball-and-stick model; right: van der Waals representation; the unit cell is outlined.

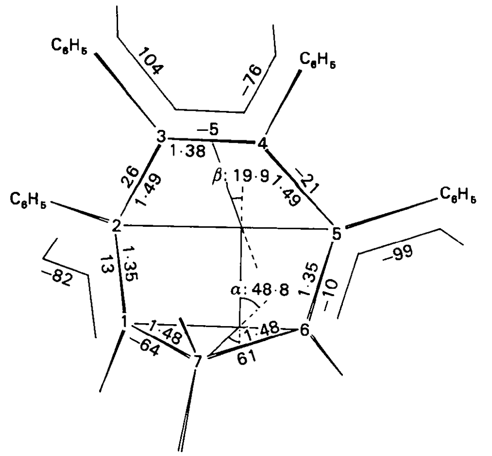

Fig. 5. Dihedral angles (°) and bond lengths (Å) from a single-molecule calculation.

the gaps between these rings are broadened and the rings are rotated to a more horizontal position in relation to the heptatriene moiety. With these effects on the molecular geometry taken into account in an *MCA* calculation of the crystal packing, the experimental structure is nicely reproduced.

Fig. 6 shows the results; the phenyl rings are rotated in a similar way as in the experimental structure and β is increased to 36°. Comparison of these β angles with the angles reported for 2,5-dimethyl-3,4-diphenyl-1,3,5-cycloheptatriene (Stegemann & Lindner, 1979) (β calculated for the isolated molecule = 27·5; β calculated for the packed moleculed = 31·9; β exp. = 34·3°) shows that the isolated calculation predicts a significant diminishing of β if one changes the methyl groups to phenyl in contrast to the experimental results

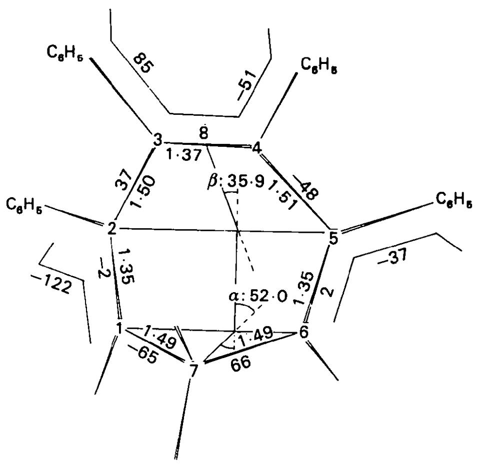

Fig. 6. Dihedral angles (°) and bond lengths (Å) from a packed-molecule calculation.

for the molecules in the crystals. Hence, it requires much care to analyse and interpret experimental and theoretical results. The asymmetry at the tip cannot be reproduced in the calculation; α, however, is increased to 52° to avoid the close contact between C(7) and C(43). The energy difference between the structures of the isolated and packed molecule has been estimated to be 5 kJ mol^{-1}, negligible in comparison with the calculated sublimation enthalpy of 187 kJ mol^{-1}. The inversion barrier between the two boat forms has been calculated to be 64 kJ mol^{-1} (*PIMM*) in agreement with the observed $\Delta G^* = 65{\cdot}7$ kJ mol^{-1} (Kessler, 1980). The enthalpy difference between the heptatriene and the isomeric norcaradiene structure is estimated to be about 50 kJ mol^{-1}.

The calculations were carried out at the Rechenzentrum der Technischen Hochschule Darmstadt. We thank Professor H. Kessler for supplying the crystals and Professor A. Warshel for a copy of the *MCA* program. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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The Structures of α- and β-Parachloral [2,4,6-Tris(trichloromethyl)-1,3,5-trioxane]

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Abstract

Orthorhombic crystals of the α isomer, $C_6H_3Cl_9O_3$, $(CCl_3CHO)_3$, belong to the space group *Pnma* with $a = 10{\cdot}666$ (2), $b = 15{\cdot}439$ (1), $c = 9{\cdot}400$ (1) Å, $Z = 4$; monoclinic crystals of the β isomer belong to the space group $P2_1/c$ with $a = 13{\cdot}115$ (4), $b = 5{\cdot}887$ (1), $c = 20{\cdot}064$ (7) Å, $\beta = 100{\cdot}88$ (2)°, $Z = 4$. The structures were refined to $R = 0{\cdot}070$ (α isomer) and 0·072 (β isomer). The molecular conformations of α- and β-parachloral are boat and chair forms respectively, with all three trichloromethyl substituents in the equatorial positions. In the trioxane ring of each isomer the bond lengths and angles are similar, the mean values being C—O = 1·407 Å, and C—O—C = 110·7, O—C—O = 110·4°.

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