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Anion complexes between a macrocyclic cyclophane and squaric acid: the crystal structure reveals the ideal receptor topology ordered by the substrate

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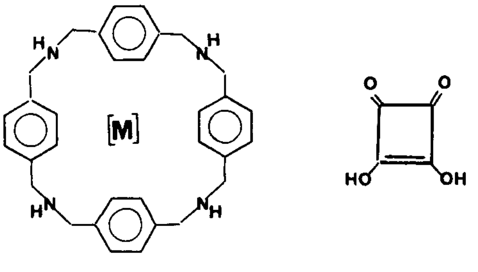
The expected [1:2] complex between a tetraprotonated tetraazaparacyclophane and squaric acid is not formed and the ligand undergoes drastic deformation. The peculiar features of this structure is the coexistence, in the same crystal cell, of 2 types of crystal lattice inclusions, corresponding to 2 different dissociation modes of squaric acid.

INTRODUCTION

Anion coordination and molecular recognition of anionic substrates play an important role in chemistry as well as in biological processes.[1] During the last few years, Jean-Marie Lehn[2] and his group have successfully synthetized different classes of anion receptors. More specifically, macrocyclic polyammonium ligands revealed good affinity for anion binding.[3]

The tetrazaparacyclophane [M], fully protonated, exhibits good ability to complex square and octahedral anions.[4]



Scheme 1

The squarate complex of [M] was prepared by treatment of $[M].4H^+$ with p-TsOH (2 eq) and squaric acid (1 eq) in MeOH, at reflux temperature.[4] Its NMR spectrum showed 2 p-toluene sulfonates per ligand, indicating the formation of a [1:1] complex with the squarate anion. These observations together with considerations of size and shape complementarity between $[M].4H^+$ and squarate anion led to the proposed structure **1** for this complex (Fig 1a).

By treatment of the $[M].4H^+$ ligand with an excess of squaric acid (2 eq), complexation of the molecular receptor is observed in D_2O. Suitable crystals were obtained and an X-ray structure determination of the latter complex was undertaken to investigate the anchorage of the squarate guest with the polyammonium ligand.

It was expected that the 4 $(NH_2)^+$ groups of macrocycle $[M].4H^+$ would bind 2 squarate ions, located on each side of the mean plane of [M], as shown on Figure 1b. In these postulated arrangements, the molecular complex would be [1:2]. Indeed, the crystallographic results are different and exhibit a very interesting structure.

RESULTS AND DISCUSSION

The first information from this crystal structure is that one single cyclophane does not form a [1:1] nor a [1:2] complex with squarate anion. Several cyclophane molecules form extramolecular cavities, where guest anions are inserted, so that two supramolecular associations, with [4:1] and [3:1] stoichiometries, are observed.

The ligand

It is interesting to point out the distorsion of the macrocycle from a square planar formula to a triangular shape (Fig 2): this is shown dramatically by the dihedral angles between the phenyl rings: two

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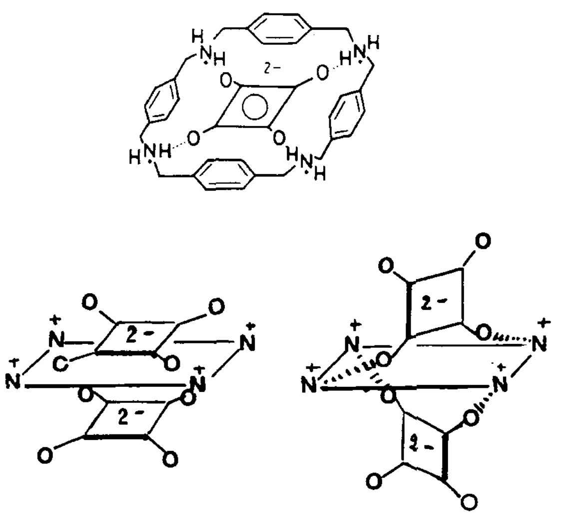

Figure 1 (a) Possible complexation between one squarate anion and one protonated cyclophane. (b) Two possible complexes between two squarate anions and one macrocycle.

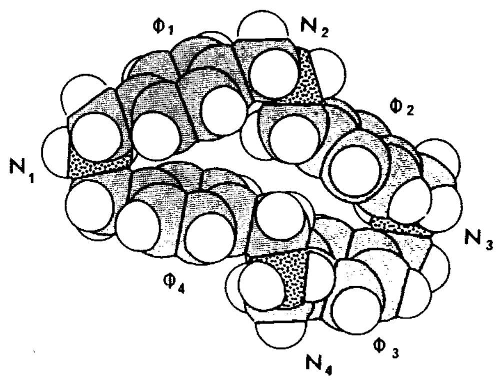

Figure 2 Flattened shape of the cyclophane.

rings are practically coplanar (8°) forming the triangle basis. The facing dihedral angle is 124°. And the two other angles are equal to 28° each. This isocel shape puts the two phenyl rings at each apex in close contact (closest approach: 3.1 Å).

The anions

The distribution of the anions forms two different crystal lattice inclusions, imbricated one into the other. The coexistence in the same cell of the two kinds of arrangement reveals two guest-specific spaces corresponding to the two different anionic entities observed in the crystal structure.

In cavity I, one squarate dianion $[C_4O_2]^{2-}$, fully dissociated, is encapsulated in an arrangement of four macrocycles. In each one, the binding site is a different protonated nitrogen.

In cavity II, negative charges are believed to be delocalized between two bonded squaric molecules. The anionic dimer is inserted between three macrocycles, the binding site being one $(NH_2)^+$ group in each one.

These results are not surprising, if we take into account the peculiar behaviour of squaric acid. In contrast to squarate dianion $[C_4O_4]^{2-}$, considered as an aromatic anion, $H_2C_4O_4$ was found[5] to contain partially localized double bonds in the four-member ring. The strong hydrogen bonding in $H_2C_4O_4$ suggests that highly associated $[H_2C_4O_4]_n$ aggregates might exist in solution and proton dissociation could proceed stepwise:

$$[H_2C_4O_4]_n \rightarrow mH^+ + H_{2-m}[C_4O_4]_n^{m-}$$

For the dimer inclusion in cavity II, we can imagine proton dissociation as follows:

$$[H_2C_4O_4]_2 \rightarrow 3H^+ + H[(C_4O_4)_2]^{3-}$$

So in the centrosymmetric crystal cell exist:

two ligands fully protonated,
five squaric acids divided as follows:
  one monomer: $[C_4O_4]^{2-}$
  two dimeric anions $[H(C_4O_4)_2]^{3-}$.

The monomer is located on the center of symmetry. In the entire cell, 18 water molecules, distributed on 26 sites, some of them being not fully occupied, complete the organization of the hydrogen bonding.

Monomer environment

Each oxygen of the monomeric dianion is H-bonded to a $(NH_2)^+$ group belonging to four different macrocyclic units (Figure 3a). We can consider these four protonated subunits as forming the ligand [L] of a [1:1] complex (see Fig. 3b). This architecture suggests an ideal receptor model, based on the same binding sites but with a more suitable shape and size (7 × 5 Å) than $[M].4H^+$. The complete anchorage of the dianion is maintained by an array of eight hydrogen bonds (two per oxygen atom of the anion), directed to the four nitrogen and to four water molecules (Table 1). There is a stacking effect between the monomeric dianion between two phenyls of centrosymmetrically related cyclophanes.

The hydrogen atoms of the water molecules have not been determined by X-ray analysis. However, their positions have been deduced taking into account the distance and the angles between the respective nature of donors and acceptors in the crystal packing.

Dimer environment

In the crystal cell, the four other squaric acids are interconnected 2 by 2 through a strong hydrogen bond (2.52 Å). Each dimer is externally linked to three

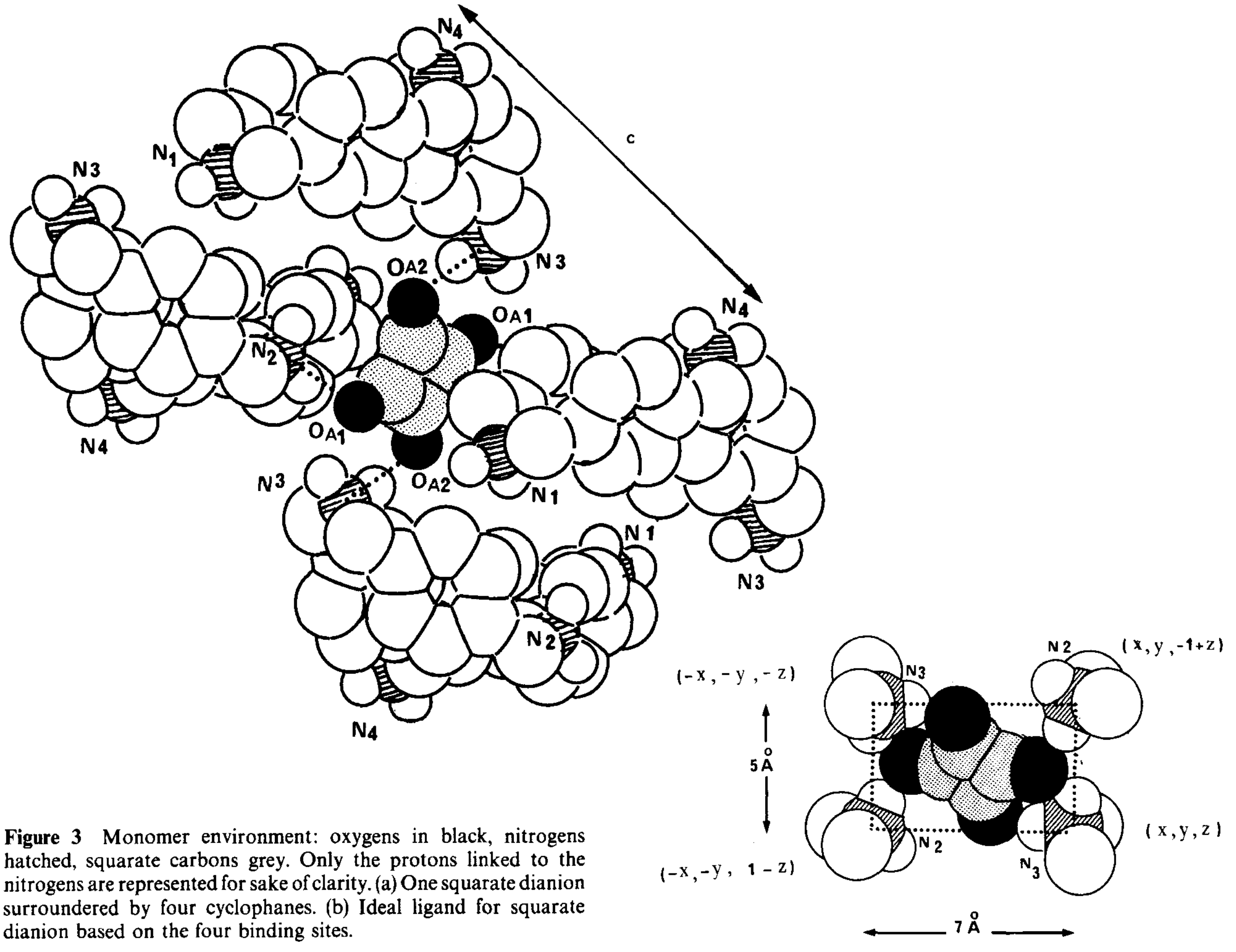

Figure 3 Monomer environment: oxygens in black, nitrogens hatched, squarate carbons grey. Only the protons linked to the nitrogens are represented for sake of clarity. (a) One squarate dianion surroundered by four cyclophanes. (b) Ideal ligand for squarate dianion based on the four binding sites.

Table 1 Hydrogen bonding to protonated nitrogens and water molecules (W). A = Acceptor, D = Donor H theoretically positioned (N-N = 1.00 Å, <CNH = 108°)

Monomer Binding

A	H-D	A···D	A···H	<(C=O···D)	<(AHD)
OA1	H_{N2A}-N2ii	2.798(4)	1.82	118.2(3)	164°
OA1	W2	2.813(6)		130.8(3)	
OA2	H_{N3B}-N3i	2.855(5)	1.88	106.8(3)	163°
OA2	W1	2.823(5)		119.2(3)	

i = $-x, -y, -z$ ii = $x, y, -1+z$

Dimer Binding

A	H-D	A···D	A···H	<(C=O···D)	<(AHD)
O2B	O2D	2.521(5)		111.6(3)	
O1B	H_{N3A}-N3	2.835(5)	2.00	117.1(3)	140°
O3B	H_{N1B}-N1i	2.790(5)	1.83	110.4(3)	159°
O3B	W4ii	2.953(5)		124.8(3)	
O4B	W2iii	2.782(6)		169.4(3)	
O1D	W6	2.82(1)		112.8(4)	
O2D	W7	2.69(1)		127.3(4)	
O3D	W3	2.69(6)		136.8(4)	
O3D	W5i	2.76(1)		128.1(4)	
O4D	H_{N4A}-N4iv	2.75(1)	1.80	107.3(3)	160°
O4D	W9	2.69(2)		119.2(4)	

i = $x, -1+y, -1+z$, ii = $x, -1+y, z$, iii = $-x, -1-y, z$, iv = $1-x, -1-y, -z$

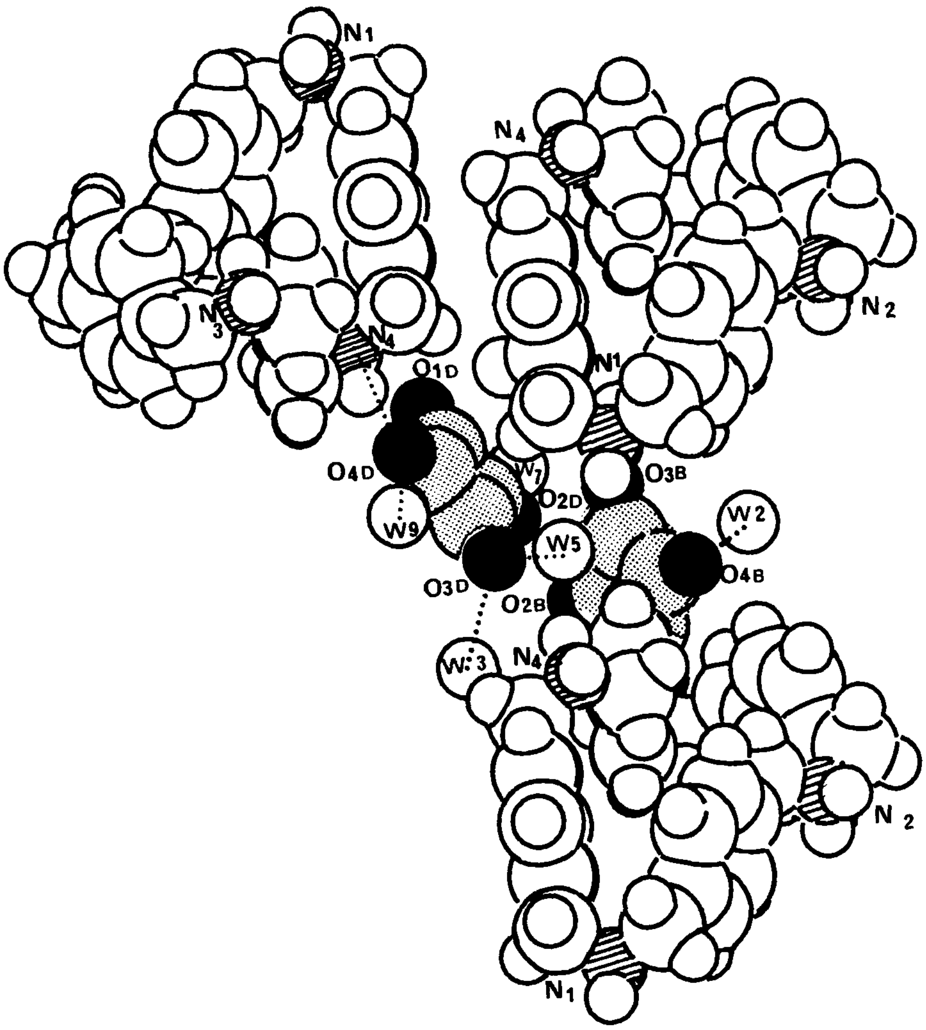

Figure 4 Dimer environment: all the hydrogens are drawn. Water molecules are included.

Table 2 Geometry of the cyclophane (Å and °) (e.s.d.: 0.01 Å, 0.1°)

Distances			*Angles*		*Phenyl dihedral angles (e.s.d. = 2°)*	
Na	N2	7.38	(N1, N2, N3)	102.4	Ph3, Ph4	8
N2	N3	7.09	(N1, N4, N3)	100.3	Ph1, Ph2	124
N3	N4	7.52	(N2, N1, N4)	52.7	Ph1, Ph4	28
N4	N1	7.16	(N2, N3, N4)	52.4	Ph2, Ph3	28
N2	N4	6.46				
N1	N3	11.28				

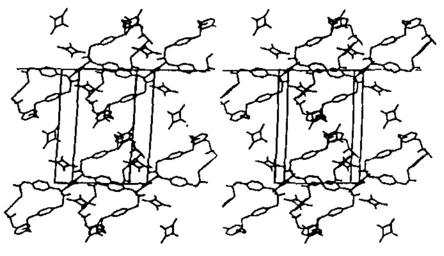

Figure 5 Stereo representation of the unit cell packing.

protonated N atoms belonging to three different cyclophanes, and seven water molecules (Fig 4, Table 2). The two planes of a dimer form a dihedral angle of 58°. Similar results have been reported in the hydrogen bond studies of dimethyl ammonium hydrogen squarate by Wang et al.[5]. In the structure of $[H_2NMe_2]^+$ $[H_3(C_4O_4)_2]^-$, the observed repeat unit is one cation and two squaric acid molecules interlinked strongly by one hydrogen atom (O–H···O: 2.435 Å) with a dihedral angle of 26°.5 between the anionic planes.

Crystal packing

The stereo view of the packing with only the ligands and the guests is displayed on Figure 5.

Table 3 Crystallographic details

Chemical Formula	$[C_{32}H_{40}N_4]5/2[O_4H_2O_4]9H_2O$
Mr	1847.86
crystal dimensions	0.4 × 0.3 × 0.2 mm
System	Triclinic
Space Group	P1
a(Å)	17.255(7)
b(Å)	12.590(5)
c(Å)	11.509(5)
α(°)	93.39(4)
β(°)	86.53(5)
γ(°)	94.08(5)
V(Å^3)	2457.43
Z	2
Dc (g·cm^{-3})	1.25
Radiation (Å)	MoKα ($\lambda = 0.7107$)
No. of reflexions measured	14311
independant	14286
observed	6734
criterion	$l > 4.5\sigma(l)$
R	0.086
Rw	0.092
w	$1/[\sigma^2(Fo) + 0.001Fo^2]$
Δ/σ	0.371
Δ/ρ(e.Å^{-3})	−0.6, +0.5

Table 4 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms. ($U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$)

	X	*Y*	*Z*	*U*
N1	2988(2)	2550(2)	8688(3)	46(3)
N2	267(2)	−2041(2)	6544(2)	39(2)
N3	1069(2)	−2753(3)	363(3)	46(3)
N4	3924(2)	−2444(2)	5115(3)	45(3)
C1	2604(3)	1697(3)	9336(4)	56(4)
C2	2223(2)	767(3)	8530(3)	43(3)
C3	1652(3)	939(3)	7782(5)	61(4)
C4	1298(3)	93(3)	7036(4)	62(4)
C5	1489(2)	−969(3)	7052(3)	39(3)
C6	2041(2)	−1140(3)	7815(3)	48(3)
C7	2411(3)	−281(3)	8543(3)	51(4)
C8	1120(2)	−1889(3)	6240(3)	46(3)
C9	−111(3)	−3062(3)	5897(3)	45(3)
C10	73(2)	−3180(3)	4588(3)	38(3)
C11	−177(3)	−2451(3)	3920(3)	49(3)
C12	−6(2)	−2580(3)	2724(3)	46(3)
C13	410(2)	−3437(3)	2148(3)	39(3)
C14	648(2)	−4172(3)	2810(3)	45(3)
C15	486(2)	−4033(3)	4017(3)	44(3)
C16	544(3)	−3614(3)	822(3)	49(3)
C17	1929(3)	−2864(4)	407(3)	58(4)
C18	2212(2)	−2765(3)	1632(3)	45(3)
C19	2556(3)	−3617(3)	1964(3)	50(4)
C20	2829(2)	−3544(3)	3095(3)	47(3)
C21	2759(2)	−2608(3)	3898(3)	41(3)
C22	2410(2)	−1751(3)	3561(3)	48(3)
C23	2146(3)	−1820(3)	2452(4)	52(4)
C24	3056(2)	−2521(3)	5121(3)	45(3)
C25	4301(2)	−1435(3)	4768(4)	45(3)
C26	4152(2)	−452(3)	5679(3)	40(3)
C27	4477(3)	−337(3)	6762(4)	52(4)
C28	4358(3)	579(3)	7603(4)	54(4)
C29	3915(2)	1380(3)	7371(4)	45(3)
C30	3593(2)	1261(3)	6254(4)	45(3)
C31	3706(2)	355(3)	5441(3)	42(3)
C32	3813(2)	2377(3)	8260(4)	50(4)
O1A	−49(2)	−1726(2)	−1014(2)	46(2)
O2A	−767(2)	572(2)	−1299(2)	61(3)
C1A	−24(2)	−770(3)	−464(3)	39(3)
C2A	−345(2)	251(3)	−585(3)	40(3)
O1B	1022(2)	−3727(2)	−2035(2)	52(2)
O2B	1921(2)	−4789(2)	−4416(2)	57(3)
O3B	2268(2)	−6858(2)	−3196(3)	53(2)
O4B	1395(2)	−5781(3)	−777(3)	67(3)
C1B	1359(2)	−4584(3)	−2333(3)	39(3)
C2B	1763(2)	−5092(3)	−3382(3)	41(3)
C3B	1924(2)	−6003(3)	−2865(3)	41(3)
C4B	1519(2)	−5523(3)	−1754(3)	45(3)
O1D	4542(3)	−7183(3)	−6146(3)	94(4)
O2D	2982(2)	−5844(3)	−5570(3)	73(3)
O3D	3620(2)	−4772(3)	−3064(4)	94(4)
O4D	5204(2)	−6061(3)	−3683(3)	75(4)
C1D	4290(3)	−6505(4)	−5304(4)	61(4)
C2D	3592(3)	−5910(3)	−5046(4)	57(4)
C3D	3891(3)	−5422(3)	−3929(4)	59(4)
C4D	4594(3)	−5998(3)	−4191(4)	56(4)
W1	−684(2)	−393(3)	−3693(3)	80(4)
W2	−1283(2)	−3317(3)	−1283(3)	83(4)
W3	3639(4)	−2622(4)	−2396(4)	131(7)
W4	1985(3)	1633(5)	−5398(4)	115(6)
W5	3245(4)	4857(5)	9209(7)	157(9)
W6*	3349(7)	−8576(9)	−7226(8)	120(13)
W7*	2579(8)	−6951(10)	−7674(11)	201(19)
W8*	4310(10)	−1668(9)	−264(8)	177(21)
W9*	5487(7)	−4708(16)	−1667(10)	214(25)
W10*	4059(11)	−9698(13)	784(11)	222(26)
W11*	4474(7)	−3741(11)	227(17)	195(24)
W12*	3296(8)	4005(14)	10703(15)	211(24)
W13*	4334(12)	1999(16)	1623(17)	262(34)

* f = 0.5

CONCLUSION

The distorsion of the empty host is indeed influenced by packing considerations (presence of numerous water molecules), difficulties of stereoelectronic complementarity between host and guest, and by preorganization of the binding site prior to complexation. An unexpected result of this crystal structure is to provide an insight into the structural features of squarate anion coordination; in this case, the existence and binding properties of two different anionic species are analysed in terms of receptor-substrate complementarity.

EXPERIMENTAL SECTION

A single crystal was sealed in a glass capillary and mounted on a Philips PW1100 automatic diffractometer. The experimental details are given in Table 3. The data collection was with $\Theta - 2\Theta$ mode. The intensities were corrected for Lorentz-polarisation, and for absorption.[7] The structure was solved by direct methods using the SHELXS86 program.[8] The geometrically constrained hydrogen atoms (C–H: 1.00 Å) were given the isotropic B value of the bonded atoms. All non-hydrogen atoms were refined anisotropically with the SHELX76 program.[9] Final atomic coordinates are listed in Table 4.

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