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Crystal and molecular structure of mesogenic 4-ethoxy-3′-(4-ethoxyphenyliminomethyl)-4′-(4-methoxy-benzoyloxy)azobenzene[†]

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4-Ethoxy-3′-(4-ethoxy-phenylimino-methyl)-4′-(4-methoxy-benzoyloxy)-azobenzene (EEMA) exhibits liquid crystalline behaviour despite the strong deviation of the molecule from both rod-like and disc-like shape. In order to obtain further information about EEMA the compound was resynthesized and a single-crystal X-ray analysis was performed. EEMA crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The structure was solved by direct methods and refined to $R = 0{\cdot}058$ ($R_w = 0{\cdot}055$) for 2473 observed reflections. The EEMA molecule has a bifurcated shape. The phenyliminomethyl branch is bent markedly from the nearly linear three-ring basic fragment but is almost coplanar with the azobenzene moiety. The molecular conformation is apparently affected by an intramolecular interaction of the carboxylic and azomethine group (close C . . . N contact distance of 2·783(5) Å). The molecular packing in the crystal can be described in terms of a sheet structure with interdigitating comb-like rows of molecules within the sheets.

1. Introduction

In a systematic investigation of the relationship between structure and properties, Weissflog and Demus [1, 2] were able to show that the suppression of the liquid-crystalline properties of a compound by large lateral substituents is smaller than previously expected. Recently, we reported [3] that even cyclic segments may be bound to the middle moiety of three-ring compounds without the loss of the liquid-crystalline properties. The clearing temperatures are unexpectedly high if the laterally attached ring system is bound to the basic mesogen by a spacer with an odd number of single segments. The space-filling models of these compounds show that the molecules are neither rod-like nor disc-like. Simply considering the length to breadth ratio of these molecules does not provide a convincing explanation of the occurrence

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[†] Thermotropic liquid-crystalline compounds with lateral long chain substituents: Part X.
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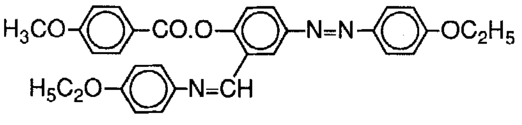
of anisotropic liquid phases. The X-ray investigation of the smectic A phases of 4-nitrobenzyl 2,5-bis-(4-*n*-alkoxy-benzoyloxy)-benzoates has already revealed pecularities; the layer thickness is considerably smaller than the length of the basic molecule [4].

Due to the lack of single crystals suitable for X-ray analysis, no details concerning the molecular structure or the arrangement of mesogenic compounds with large lateral substituents in the crystalline state and, hence in the liquid-crystalline state, have been reported until now.

In the literature there are few examples of laterally aryl-substituted compounds which are discussed in terms of their liquid-crystalline properties. Critical reviews are given in [3, 5]. The data given by Kuhrmann [6] are especially interesting since they point at liquid-crystalline compounds with laterally attached aromatic groups†. One of these compounds, 4-ethoxy-3′-(4-ethoxyphenyliminomethyl)-4′-(4-methoxybenzoyloxy)-azobenzene (EEMA) has been resynthesized;



Details of this synthesis are described in §3 of this paper. EEMA shows the transition temperatures,

$$C_1 \quad 155°C \quad C_2 \quad 160°C \quad (N \quad 73°C) \quad I,$$

whereas Kuhrmann [6] reported the data C 145°C (N 59°C) I. Our transition temperatures may be higher due to the better purification methods applied.

In contrast to many previous unsuccessful attempts to prepare suitable single crystals of mesogens with longer lateral substituents, recrystallization from ethanol yielded such specimens of EEMA. Thus the possibility for an accurate determination of molecular structure (including conformational behaviour) and packing in the solid state of a laterally aryl-substituted compound was provided.

2. Crystal and molecular structure

The molecular structure of EEMA including the applied atom labelling is illustrated in the ORTEP drawing [9] shown in figure 1. A realistic picture of the molecular shape can be realized by the space-filling PLUTO model [10] using the van der Waals radii given by Bondi [11] for plotting the atom contours shown in figure 2. Essential parameters of the molecular geometry are summarized in tables 1 and 2.

The most striking feature of the molecular shape of EEMA is that it is neither rod-like nor disc-like but can be described as distinctly bifurcated or like a slightly deformed *Y*. For a more detailed discussion of the molecular conformation, the EEMA molecule shall be considered as consisting of three structural fragments sharing the central phenyl ring: (i) an azobenzene, (ii) a phenylbenzoate and (iii) a benzylideneaniline moiety.

A reasonable number of X-ray crystal structure determinations have shown that azobenzene and its 4,4′-disubstituted derivatives are completely or essentially planar

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† By mistake the substituents have been exchanged in the tables given by Kast [7] from which the data were transcribed in the tables [8] so that the data for compounds Numbers 2522–2527 and 2589–2590 are not correct.

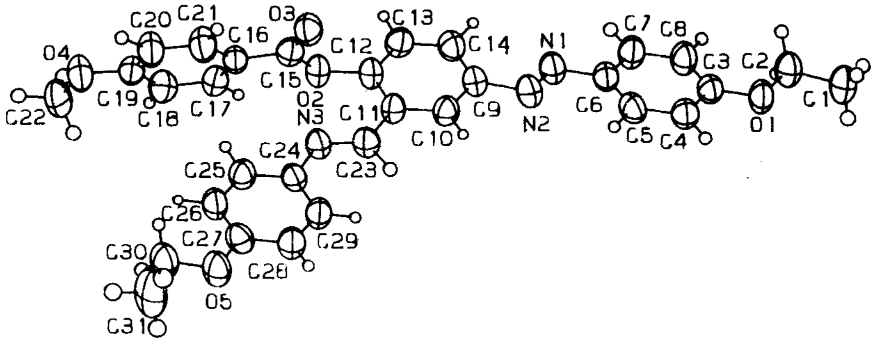

Figure 1. ORTEP drawing [9] of the EEMA molecule with the atom labelling used in the X-ray analysis (thermal ellipsoids at the 50% probability level, arbitrary size of hydrogen atoms).

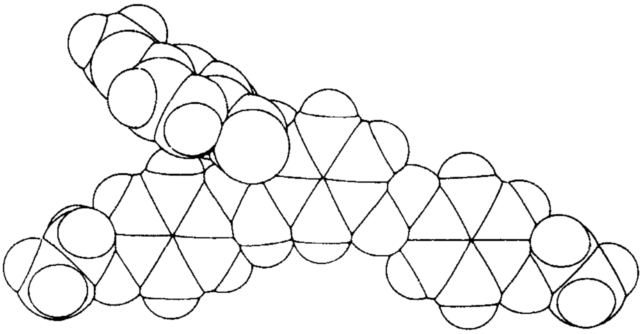

Figure 2. Space-filling PLUTO plot [10] of the EEMA molecule (atom spheres according to van der Waals radii [11]).

in the solid state. Despite the additional substitution in the m-position of one phenyl ring these results are confirmed by the observed conformation of the azobenzene moiety in EEMA. Its C–N=N–C central part is exactly planar (cf. the corresponding torsion angles in table 2) and inclined to the neighboring phenyl rings I (C3 . . . C8) and II (C9 . . . C14) by 1·8° and 9·5°, respectively.

The phenylbenzoate moiety also adopts largely the expected conformation. The orientation of the carboxylic group with respect to the O- and C-bonded adjacent phenyl rings II and III (C16 . . . C21) can be described by the interplanar angles of 78·2° and 5·4°, respectively, as well as by the corresponding torsion angles given in table 2. All these values agree well with the results of experimental and theoretical conformational analyses performed for substituted phenylbenzoates reported earlier [12].

In contrast to the azobenzene and phenylbenzoate moieties showing normal conformational behaviour the benzylideneaniline part of the EEMA molecule exhibits a conspicuous pecularity. It is essentially planar (within 0·07 Å) and the twist of the N–C and C–C bonded phenyl rings with respect to the plane of the central four-atom azomethine group (C11, C23, N3, C24) is very small. The corresponding interplanar angles are 5·1° and 1·9°, respectively. But as a result of both theoretical studies and experimental work, a marked non-planarity has been proved to be the preferred conformation of benzylideneanilines [13]. *Ab initio* calculations indicated that the

Table 1. Selected bond lengths and angles with estimated standard deviations in parentheses.

Atoms	Bond length/Å	Atoms	Angle/°
Ethoxy group I			
C1–C2	1·502(6)	C1–C2–O1	107·5(5)
C2–O1	1·436(5)	C2–O1–C3	117·3(5)
O1–C3	1·369(5)	O1–C3–C4	116·1(5)
Azo group			
C6–N1	1·432(5)	C5–C6–N1	125·1(5)
N1–N2	1·249(5)	C6–N1–N2	115·1(5)
N2–C9	1·446(5)	N1–N2–C9	112·3(5)
		N2–C9–C10	115·9(5)
Carboxylic group			
C12–O2	1·412(5)	C12–O2–C15	117·0(4)
O2–C15	1·357(7)	O2–C15–O3	123·2(5)
O3–C15	1·211(6)	O2–C15–C16	112·3(4)
C15–C16	1·484(5)	O3–C15–C16	124·4(6)
Methoxy group			
C19–O4	1·382(5)	C18–C19–O4	124·6(5)
O4–C22	1·438(7)	C19–O4–C22	116·7(5)
Azomethine group			
C11–C23	1·477(6)	C12–C11–C23	126·0(5)
C23–N3	1·262(5)	C11–C23–N3	123·7(5)
N3–C24	1·426(5)	C23–N3–C24	121·0(5)
		N3–C24–C25	116·5(5)
Ethoxy group II			
C27–O5	1·375(5)	C26–C27–O5	124·2(6)
O5–C30	1·433(6)	C27–O5–C30	118·5(5)
C30–C31	1·503(7)	O5–C30–C31	107·2(5)
Mean values for phenyl rings			
Ring I (C3 . . . C8)			
C–C	1·385(9)	C–C–C	120·0(9)
Ring II (C9 . . . C14)			
C–C	1·388(6)	C–C–C	120·0(2·4)
Ring III (C16 . . . C21)			
C–C	1·384(8)	C–C–C	120·0(1·9)
Ring IV (C24 . . . C29)			
C–C	1·385(8)	C–C–C	120·0(1·4)

minimum energy conformation corresponds to a rotation about the N-phenyl bond of 45° and a rotation about the C-phenyl bond of 0° [13]. A large number of benzylideneanilines examined by X-ray analysis are more or less consistent with these values. Some exceptions which are planar, or nearly so, such as 4-(4,4,4-trifluorobutyl)-N-(4-trifluoromethoxybenzylidene)-aniline [14], bis-(4-nonyloxybenzylidene)-1,4-phenylenediamine [15], ethyl 4-(4-methoxybenzylideneamino)cinnamate [16] and 4-chloro-N-(4-chlorobenzylidene)-aniline in its triclinic form [17], are explained by the effect of packing forces. Our explanation for the planarity of the benzylideneaniline moiety in EEMA is based on the short intramolecular N3 . . . C15 contact distance of 2·783(5) Å which is considerably smaller than the sum of the van der Waals radii of nitrogen and carbon (3·25 Å [11]). As suggested by several authors (see, for example, [13, 18]), one of the factors responsible for the significant twist around the

Table 2. Selected torsion angles.

Atoms	Angle/°	Atoms	Angle/°
C2–O1–C3–C4	−176·9(5)	O2–C15–C16–C17	−3·6(7)
C5–C6–N1–N2	0·2(8)	O3–C15–C16–C17	173·4(6)
C6–N1–N2–C9	−178·7(5)	O2–C12–C11–C23	−7·2(8)
N1–N2–C9–10	170·9(5)	C18–C19–O4–C22	6·0(8)
C11–C12–O2–C15	74·7(6)	C10–C11–C23–N3	−178·8(5)
C12–O2–C15–C16	−170·3(5)	C11–C23–N3–C24	−179·4(5)
C12–O2–C15–O3	12·7(8)	C23–N3–C24–C25	175·7(5)
		C26–C27–O5–C30	−8·4(8)

N-phenyl bond generally observed is to enable an interaction of the nitrogen lone pair electrons with the π-system of the aniline ring; this delocalization would be essentially zero for a planar conformation. In EEMA, however, the close interatomic contact indicates an intramolecular interaction between carbon atom C15 carrying a positive partial charge and nitrogen atom N3 in which the lone pair electrons of the latter are involved. In this case the conjugation of the π-electron systems of the azomethine group and its two neighbouring phenyl rings is the predominant factor, which is maximized for a planar conformation. The assumption of such an extended π-electron delocalization is supported by the experimental result that in EEMA the three phenyl rings I, II and IV (C24 . . . C29) bridged by the azo and azomethine groups, respectively, are approximately coplanar (interplanar angles I/II 10·8°, II/IV 3·4°, I/IV 9·2°). The ethoxy groups are also approximately coplanar with the phenyl rings to which they are attached (interplanar angles of 2·7° and 10·7° for rings I and IV, respectively).

The marked coplanarity of the 4-ethoxyazobenzene moiety belonging to the three-ring basic molecule with the lateral aromatic substituent attached by the azomethine spacer group is a striking feature of the molecular structure of EEMA and can be clearly seen in figures 1 and 2. On the other hand, this planar fragment is inclined strongly to the remaining segment, namely the benzoate moiety. The angle between the normals to the least-squares planes defined by the non-hydrogen atoms of the phenyliminomethyl-azobenzene fragment (without the alkyl groups) and the benzoyloxy fragment (without the methyl group) is 76·8°.

All the observed bond lengths and angles of EEMA are approximately as expected and hence, do not warrant further comment. All four phenyl rings are planar within 0·02 Å. The C–H bond lengths, range from 0·90(4) to 1·22(4) Å (mean 1·01(7) Å).

The crystal packing is characterized by a perfectly parallel alignment of the molecular long axes generated by the three lattice translations and the inversion centres of the space group. A further striking feature of the crystal structure is the formation of sheets of molecules with an orientation approximately perpendicular to [001]. In figure 3 a cross-section through five such sheets is shown. Within the sheets the molecules are related by inversion centres and translations along [$\bar{1}\bar{1}$0] and [211], respectively. As can be seen in figure 4, the molecules of one sheet are arranged in rows with their long axes end to end. Since the lateral aromatic branches are also aligned parallel to each other but inclined considerably to the long axes of the basic molecules the rows can be referred to as comb-like. Neighbouring rows are interdigitated in pairs by the lateral branches. The holes between the azobenzene and benzylidene-aniline moieties of two neighbouring molecules in one sheet evident in figure 4 are in reality occupied by parts of the benzoate fragments protruding from the two adjacent sheets. In this way neighbouring sheets are interlocked.

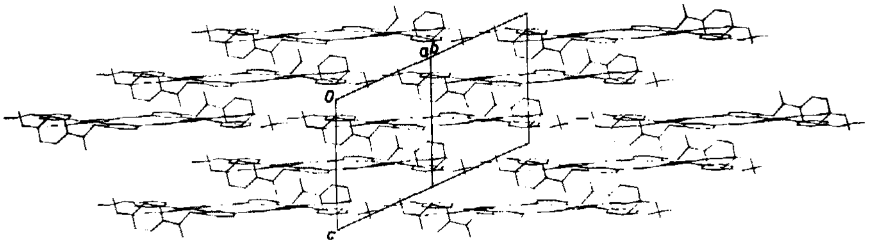

Figure 3. PLUTO plot of the crystal packing projected along [$\bar{1}10$] showing five sheets of molecules.

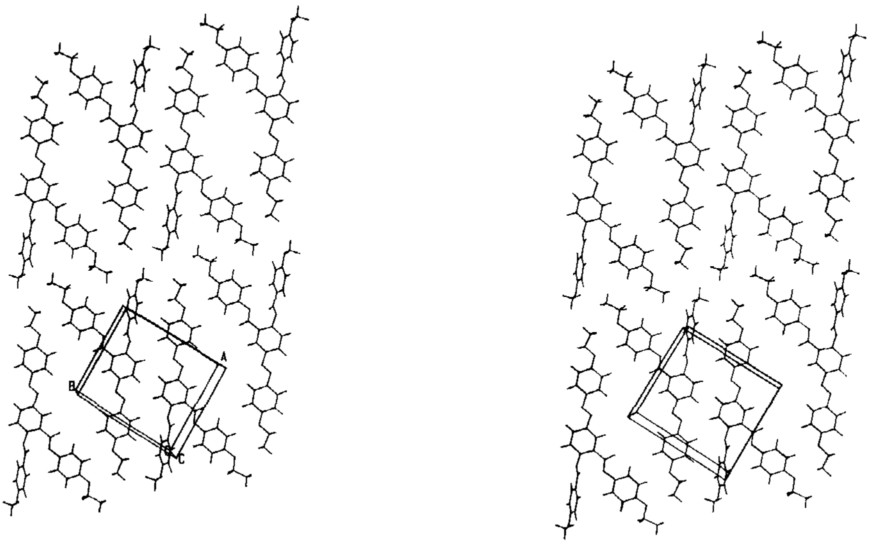

Figure 4. Stereo PLUTO plot of one sheet of molecules in the crystal structure of EEMA projected along [001].

Table 3. Intermolecular contact distances shorter than the sum of the appropriate van der Waals radii [11].

From atom in x, y, z	To atom	In position	Distance/Å
N3	C15	x, y, z	2·783(5)
N3	C22	$-x, -y, -z$	3·145(7)
C17	H80	$1-x, 1-y, 1-z$	2·70(3)
C18	H80	$1-x, 1-y, 1-z$	2·89(3)
C20	H210	$-x, -y, 1-z$	2·84(4)
C21	H210	$-x, -y, 1-z$	2·70(4)
O3	H40	$x-1, y, z$	2·69(3)
O3	H200	$-x, -y, 1-z$	2·59(4)
O3	H230	$1-x, -y, 1-z$	2·53(4)
O5	H12	$2-x, -y, 1-z$	2·68(4)
H11	H221	$2+x, 1+y, 1+z$	2·30(5)
H221	H221	$-1-x, -y, -z$	2·35(5)

In table 3 the relevant intermolecular contacts in the crystal structure of EEMA are listed. In most of them hydrogen atoms participate. There is no indication of other than normal van der Waals forces.

The observed structure of EEMA confirms our conclusion drawn from model considerations [3] that liquid-crystalline compounds with aromatic branches represent a special type of laterally substituted mesogens. The liquid-crystalline behaviour of EEMA cannot be interpreted in terms of the statistical theories of liquid crystals for rod-like [19], disc-like [20] or lath-like [21] molecules. Obviously a new theoretical approach is required to explain the mesophases found in compounds deviating from the classical molecular shapes.

3. Experimental

3.1. *Synthesis*

EEMA was synthesized according to the synthetic route described by Kuhrmann [6]. Salicyl aldehyde was coupled with diazotised 4-ethoxy-aniline and then, the phenolic hydroxy group of the 4-ethoxy-3′-formyl-4′-hydroxy-azobenzene was acylated with 4-methoxy-benzoyl chloride in toluene and triethylamine as base. The 4-ethoxy-3′-formyl-4′-(4-methoxy-benzoyloxy)-azobenzene (recrystallized from CCl_4) has liquid-crystalline properties (C 140°C N 253°C I). The condensation of the formyl compound with 4-ethoxy-aniline in boiling ethanol yielded EEMA, which was purified by column chromatography using Al_2O_3 (Al_2O_3 after Brockmann, activity II–III, elution with $CHCl_3$). Multifold recrystallization from ethanol delivered the pure product which was checked by thin layer chromatography with SILUFOL plates (solvent system benzene/methanol 95 : 5).

3.2. *Crystal structure determination*

Needle-shaped orange crystals of EEMA were obtained by recrystallization from ethanol and cut to give specimens suitable for X-ray diffraction investigations. Experimental details and relevant crystal data are given in table 4. The structure was

Table 4. Crystal data and details of intensity measurements and structure refinement.

Molecular formula and weight	$C_{31}H_{29}N_3O_5$, 523·6 g mol^{-1}
Crystal system and space group	triclinic, $P\bar{1}$
Cell parameters	$a = 10{\cdot}979(5)$, $b = 12{\cdot}427(7)$, $c = 11{\cdot}048(5)$ Å $\alpha = 110{\cdot}83(4)$, $\beta = 105{\cdot}81(4)$ $\gamma = 82{\cdot}98(4)°$ $V = 1355{\cdot}0(1{\cdot}1)$ Å^3, $Z = 2$, $F(000) = 552$ $D_c = 1{\cdot}283$ g cm^{-3}
Radiation	CuKα, $\lambda = 1{\cdot}54178$ Å (graphite monochromator)
Temperature	291 K
μ(CuKα)	6·8 cm^{-1}
Crystal size	0·10 × 0·25 × 0·45 mm
Intensity data collection	Syntex P2_1 diffractometer, $\theta/2\theta$ scan, bisecting mode, $2\theta \leqslant 115°$, *hkl* range: 0, $\bar{1}\bar{3}$, $\bar{1}\bar{2}$ to 11, 13, 12
Standard reflections (max. Δ)	$20\bar{1}$ (2·6%), $0\bar{2}2$ (1·8%)
No. of measured reflections	3533
No. of observed reflections	2473 with $I \geqslant 1{\cdot}96\sigma(I)$
No. of reflections/parameter	5·3
Final R (R_w)	0·058 (0·055)
$(\Delta/\sigma)_{max}$ in final LS cycle	0·264
Maximum and minimum heights in final $\Delta\varrho$	$+0{\cdot}154$ and $-0{\cdot}193\,e$ Å^{-3}, respectively

Table 5. (*a*) Final fractional coordinates ($\times 10^4$) and isotropic equivalents (Å^2, $\times 10^3$) of the anisotropic displacement parameters for the non-hydrogen atoms. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
C1	14652(4)	6802(4)	8249(5)	86(3)	C21	207(4)	248(4)	3616(4)	78(3)
C2	13244(4)	6678(4)	7916(5)	73(3)	C22	−3279(4)	−146(4)	−186(5)	86(3)
C3	11769(4)	5159(4)	7091(4)	61(2)	C23	4761(4)	3(4)	3350(4)	61(2)
C4	11568(4)	3984(4)	6704(5)	68(3)	C24	3557(4)	−1651(4)	2199(4)	54(2)
C5	10346(4)	3587(4)	6315(4)	69(3)	C25	2338(4)	−2051(4)	1728(4)	63(2)
C6	9320(4)	4371(4)	6338(4)	60(3)	C26	2090(4)	−3220(4)	1134(5)	66(3)
C7	9539(4)	5524(4)	6725(5)	72(3)	C27	3084(4)	−4004(4)	996(4)	62(2)
C8	10752(4)	5927(4)	7105(5)	72(3)	C28	4311(4)	−3621(4)	1422(5)	70(2)
C9	6496(4)	2773(4)	5158(4)	56(2)	C29	4553(4)	−2459(4)	2012(5)	68(3)
C10	6201(4)	1625(4)	4543(4)	60(2)	C30	1726(4)	−5630(4)	173(5)	82(3)
C11	4958(4)	1253(4)	4018(4)	54(2)	C31	1895(5)	−6915(4)	−183(6)	127(4)
C12	4009(4)	2110(4)	4176(4)	54(2)	N1	8018(3)	4072(3)	5947(4)	66(2)
C13	4283(4)	3263(4)	4823(4)	62(3)	N2	7829(3)	3019(3)	5567(4)	64(2)
C14	5530(4)	3601(4)	5332(4)	64(3)	N3	3684(3)	−435(3)	2818(3)	59(2)
C15	2140(4)	1298(4)	4094(5)	59(3)	O1	13004(3)	5470(3)	7448(3)	75(2)
C16	872(4)	892(4)	3237(4)	54(2)	O2	2724(3)	1849(2)	3555(3)	60(2)
C17	333(4)	1120(4)	2066(5)	61(3)	O3	2590(3)	1197(3)	5179(3)	70(2)
C18	−873(4)	729(4)	1303(4)	63(3)	O4	−2728(3)	−292(3)	1087(3)	81(2)
C19	−1521(4)	114(4)	1734(5)	61(2)	O5	2950(3)	−5178(3)	455(3)	83(2)
C20	−990(4)	−148(4)	2892(5)	77(3)					

(*b*) Final fractional coordinates ($\times 10^3$) and isotropic displacement parameters (Å^2, $\times 10^2$) for the hydrogen atoms.

Atom	x/a	y/b	z/c	U_{iso}	Atom	x/a	y/b	z/c	U_{iso}
H11	1483(4)	770(4)	856(4)	11(2)	H210	58(3)	9(3)	444(3)	9(2)
H12	1506(4)	654(4)	896(4)	13(2)	H221	−419(4)	−55(4)	−47(4)	12(2)
H13	1496(4)	638(4)	748(4)	13(2)	H222	−350(4)	73(4)	−2(4)	14(2)
H21	1284(3)	707(3)	875(4)	10(2)	H223	−267(4)	−52(4)	−77(4)	13(2)
H22	1282(3)	703(3)	733(4)	8(2)	H230	562(3)	−52(3)	324(4)	12(2)
H40	1233(3)	343(3)	663(4)	9(2)	H250	163(3)	−147(3)	192(3)	7(1)
H50	1020(3)	274(3)	601(3)	8(1)	H260	122(3)	−350(3)	86(3)	5(1)
H70	877(4)	604(3)	675(4)	11(2)	H280	498(3)	−414(3)	134(3)	8(1)
H80	1088(3)	680(3)	741(3)	8(2)	H290	541(3)	−220(3)	229(3)	7(1)
H100	688(3)	108(3)	444(3)	6(1)	H301	137(3)	−524(3)	97(4)	8(2)
H130	361(3)	385(3)	499(3)	6(1)	H302	110(4)	−542(3)	−62(4)	11(2)
H140	574(3)	445(3)	582(3)	7(1)	H311	103(5)	−730(4)	−50(5)	17(2)
H170	83(3)	153(3)	174(3)	7(1)	H312	223(5)	−712(5)	63(6)	22(3)
H180	−124(3)	90(3)	45(3)	7(1)	H313	226(5)	−723(4)	−96(6)	18(2)
H200	−159(3)	−74(3)	320(4)	10(2)					

solved using the automatic direct methods option in program SHELXS-86 [21] with default input parameters. All 39 non-hydrogen atoms were found in an *E*-map with $R_E = 0{\cdot}21$ for 714 *E* values. After several cycles of full-matrix least-squares refinement with at first isotropic and then anisotropic displacement parameters ($R = 0{\cdot}10$) all the hydrogen atoms were localized in a difference Fourier map and subsequently refined isotropically in a separate block. For the last cycles of refinement, the weighting scheme was changed from unit weights to counter weights ($w = 1/\sigma_F^2$) and an empirical extinction correction was applied to F_c giving

$$F_{corr} = F_c(1 - 10^{-7}\chi F_c^2/\sin\theta)$$

χ refining to 4·8(3). The final R value was 0·058 (R_w = 0·055). All the calculations were performed on an IBM-PC using the program packages XTL [22], SHELXS-86 [21] and SHELX-76 [23]. The final positional and isotropic displacement parameters of the atoms are given in table 5.

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