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Preparation and mesomorphic properties of a homologous series of *N*,*N*′-(2-chloroterephthalylidene)bis(4-*n*-alkylaniline)s

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A series of *N*,*N*′-(2-chloroterephthalylidene)bis(4-*n*-alkylaniline)s (CTBAAs) were prepared and their mesomorphic behaviour characterized. None of the homologues showed smectic behaviour, but nematic behaviour with broad mesophases and rather low melting points was seen. The mesomorphic behaviour was compared with that of *N*,*N*′-(terephthalylidene)-bis(4-*n*-alkylaniline)s (TBAAs) and 4,4′-bis-(*n*-alkylbenzal)-2-chloro-1,4-phenylenediamines (BACPDs). An X-ray diffraction analysis of *N*,*N*′-(2-chloro-terephthal)bis(4-*n*-butylaniline) (CTBBA) showed that the molecules were packed in crystals forming a staggered arrangement called an 'imbricated structure'.

1. Introduction

N,*N*′-(Terephthalylidene)bis(4-*n*-butylaniline) (TBBA) is well known to exhibit many phases, including three crystalline phases [1–5]; consequently the homologous series, *N*,*N*′-(terephthalylidene)bis(4-*n*-alkylaniline)s (TBAAs), are most extensively studied as typical liquid crystalline compounds. However, it seems surprising that no report of the laterally substituted derivatives of TBAA can be found. This lack of literature may be partly due to the difficulty of obtaining the key starting materials, substituted terephthalaldehydes.

It has been reported that TBAA contrasts sharply with the isomeric compounds, 4,4′-bis-(*n*-alkylbenzal)-1,4-phenylenediamines (BAPDs) in their mesomorphic properties: thus TBAAs show a variety of smectic properties, but BAPDs show only nematic character [3]. The apparent structures of TBAAs are quite similar to those of the corresponding BAPDs, differing only in the reverse orientation of their azomethine linking groups. The different mesomorphic behaviour between these series has not been explained clearly; a minor difference in the framework structures of the molecules might affect the packing of the molecules in the liquid crystal phases. In the case of TBBA, conformation between the azomethine group and the benzene rings may play an important role in the molecular structure.

The introduction of a lateral substituent into the central benzene ring of TBBAs is expected to affect their mesomorphic properties, not only because of the disruptive effect but also because of the difference in the framework structures. Therefore in this paper, we wish to describe the preparation and the properties of the *N*,*N*′-(2-chloroterephthalylidene)bis(4-*n*-alkylaniline)s (CTBAAs), and an X-ray structural analysis of the representative compound, *N*,*N*′-(2-chloroterephthalylidene)bis(4-*n*-butylaniline) (CTBBA), since there is known to be the closest similarity between the molecular structures in the crystals and the fluid liquid crystals. This is our first report of a systematic investigation on the relationship between stereo structure and properties of liquid crystalline compounds.

2. Experimental

2.1. *Analytical methods and instrumentation*

Transition temperatures were determined on a Shimadzu Thermal Analysis Instrument (Model DSC-41) at a heating rate of 5°C min^{-1}. The textures of the liquid crystals were observed with a microscope under crossed nicols. IR spectra were recorded on a Jasc FTIR spectrometer via KBr pellet mixtures. NMR spectra were recorded on a Varian spectrometer (Model UNITY plus-300) at 300 MHz, with TMS as internal reference. Mass spectral data were obtained on a Hitachi spectrometer (Model M-80 B) by electron-impact ionization. Melting points are uncorrected.

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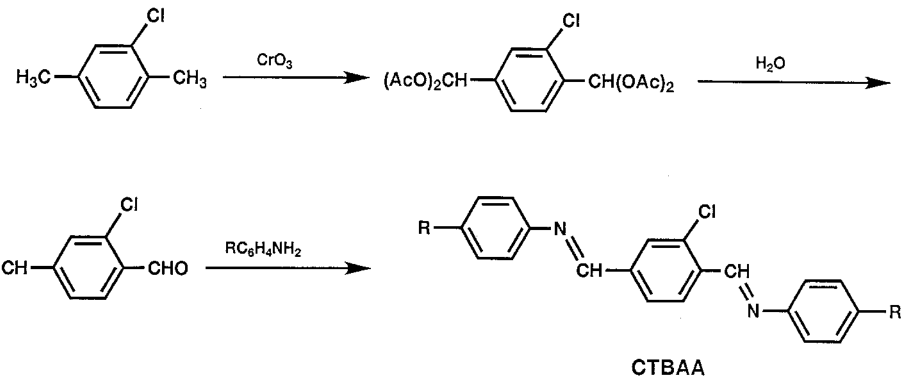


Scheme. $R \equiv C_N H_{2N+1}$ ($N = 1$–$8, 10$)

2.2. *Preparation of materials*

2-Chloro-*p*-xylene and *n*-alkylanilines were obtained from various commericial sources, and were used without further purification. The synthesis of CTBAA is illustrated in the scheme.

2.2.1. *Preparation of 2-chloroterephthalaldehyde*

To a solution of acetic anhydride (120 g, 1·18 mol) in acetic acid (56 ml), was added conc. sulphuric acid (10 ml), and then 2-chloro-*p*-xylene (5·3 g, 37·7 mmol). The suspension was cooled to 5°C, and chromium trioxide (12 g, 0·12 mol) was added in portions with rapid stirring; each addition was made only after the temperature had fallen to 10°C or lower. Stirring was continued for 4 h at 10–15°C, and the reaction mixture was poured on to crushed ice. After standing overnight at ambient temperature, the product was collected by filtration and was washed with water. Recrystallization from ethanol gave 2-chloroterephthalaldehyde tetraacetate (5·2 g, 44·7% yield, m.p. 110–112°C).

To a solution of the tetraacetate (3·09 g, 10 mmol) in ethanol (20 ml), was added 5N sulphuric acid (2 ml), and the mixture was heated under reflux for 30 min. After cooling to ambient temperature, a solid was collected by filtration and was washed with water. Recrystallization from aqueous ethanol gave 2-chloroterephthalaldehyde as colourless plates (1·53 g, 90·7% yield, m.p. 78–80°C) [6].

2.2.2. *Preparation of N,N′-(2-chloroterephthalylidene)-bis(4-n-butylaniline) (CTBBA)*

To a solution of 2-chloroterephthalaldehyde (168·5 mg, 1 mmol) in absolute ethanol, *n*-butylaniline (298 mg, 2 mmol) was added and the mixture was allowed to stir for 4 h. The completion of the reaction was ascertained by TLC. The product was collected by filtration and was recrystallized several times from absolute ethanol until a constant mesomorphic range was obtained, giving CTBBA (290 mg, 67·3% yield) as yellow plates, m.p. 50·7°C. IR ν (cm^{-1}) 2900, 2800, 1615, 1500, 1395, 1355, 1180, 1045, 840; MS *m/e* (relative intensity) 431 (40) M$^+$, 403 (100), 387 (38), 345 (29), 172 (62), 90 (29); NMR δ (in $CDCl_3$) 0·94 (6H, t, $J = 7{\cdot}4$ Hz, CH_3), 1·38 (4H, sextet, $J = 7{\cdot}4$ Hz, CH_2), 1·63 (4H, quintet, $J = 7{\cdot}4$ Hz, CH_2), 2·64 (4H, t, $J = 7{\cdot}4$ Hz, CH_2), 7·1 ∼ 7·3 (8H, m, Ar), 7·82 (1H, d, $J = 8{\cdot}2$ Hz, Ar), 7·99 (1H, s), 8·34 (1H, d, $J = 8{\cdot}2$ Hz, Ar), 8·46 (1H, s), 8·96 (1H, s). Analysis: found C 78·11, H 7·27, N 6·43; calcd C 78·03, H 7·25, N 6·50%. The transition temperatures (melting and clearing points) were 50·7 and 138·4°C.

This procedure is representative of the preparations of all the *N*,*N*′-(2-chloroterephthalylidene)bis-(4-alkylaniline)s (CTBAAs). The following CTBAAs were obtained from the corresponding 4-alkylanilines.

N,*N*′-(2-chloroterephthalylidene)bis(4-methylaniline): yield 69·1%, m.p. 139·9, c.p. 177·5°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-ethylaniline): yield 56·3%, m.p. 106·3, c.p. 164·5°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-propylaniline): yield 62·4%, m.p. 90·3, c.p. 170·0°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-pentylaniline): yield 58·4%, m.p. 54·1, c.p. 151·0°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-hexylaniline): yield 60·8%, m.p. 68·6, c.p. 129·9°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-heptylaniline): yield 56·4%, m.p. 52·8, c.p. 132·0°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-octylaniline): yield 59·8%, m.p. 57·7, c.p. 121·6°C.

N,*N*′-(2-chloroterephthalylidene)bis(4-*n*-decylaniline): yield 53·4%, m.p. 70·9, c.p. 115·6°C.

2.3. *X-ray analysis of N,N′-(2-chloroterephthalylidene)-bis(4-n-butylaniline)*

Crystals suitable for X-ray analysis were obtained by slow recrystallization from an ethanol–THF solution at ambient temperature. The data were collected at 23°C using the $\omega - 2\theta$ scan technique with a variable scan speed to a maximum 2θ value of 45°. The intensities of three representative reflections remained constant throughout the data collection, thus indicating crystal stability under X-ray irradiation. Out of the total of 6469 reflections measured, 6141 were unique. The crystal data and experimental details are listed in table 1.

The structure was solved by direct methods with MITHRIL [7]. The non-H atoms were refined with anisotropic thermal parameters, and H atoms were assigned based on the expected bonding geometry. The highest-peak in the final difference-Fourier map was 0·23 e^{-} Å^{-3}.

Table 1. Crystallographic and experimental data for CTBBA.

Formula	$C_{28}H_{31}N_2Cl$
Formula weight	431·02
Crystal system	triclinic
Space groups	$P1$, $z=4$
a	13·725(5) Å
b	21·102(9) Å
c	9·158(4) Å
α	96·25(4)°
β	107·48(3)°
γ	95·79(4)°
V	2490(2) Å^3
D_{calc}	1·150 g cm^{-3}
μ (Mo K_α)	1·27 cm^{-1}
T	296 K
$F(0\,0\,0)$	920
Crystal dimensions	0·5 × 0·3 × 0·1 mm^3
Radiation	graphite monochromated Mo K_α
R	0·069
Rw	0·080
No. of reflections used	2087 [$I > 300\sigma(I)$]
No. of parameters	559
Measurement	Rigaku AFC5R
Program system	TEXSAN
Structure determination	direct method
Refinement	full matrix least-squares

3. Results and discussion

The oxidation of 2-chloro-*p*-xylene with chromium trioxide gave the key starting material, 2-chloroterephthalaldehyde in high yield (41%) via the corresponding tetraacetate intermediate using a modification of a reported method [8]. *N*,*N*′-(2-chloroterephthalylidene)-bis(4-*n*-butylaniline) (CTBBA) and its homologues, *N*,*N*′-(2-chloroterephthalylidene)bis(4-*n*-alkylaniline)s (CTBAAs), were obtained in moderate yields from the reactions of 2-chloroterephthalaldehyde with the corresponding 4-*n*-alkylanilines.

The structure of CTBBA was elucidated by means of its IR, MS and NMR spectra. The MS spectrum showed a relatively large molecular ion peak. The NMR spectrum was consistent with the proposed structure; the proton signals of the two terminal butyl groups appeared equivalent in 300 MHz spectrum. The structures of the homologues (CTBAAs) were similarly assigned on the basis of the IR, MS and NMR spectra.

Although TBBA is known to exhibit a variety of smectic phases, CTBAAs exhibit no smectic phases, but all show nematic phases with broad mesophases. Their schlieren textures were observed through a polarizing microscope. The transition temperatures of the CTBAAs are shown in figure 1 together with those of a series of the mother compounds, *N*,*N*′-(terephthalylidene)bis-(4-*n*-alkylaniline)s (TBAAs). CTBAAs have rather low melting temperatures and significantly lower clearing temperatures (*c*. 100°C) compared with TBAAs. The range of the LC phase becomes narrow as a result of

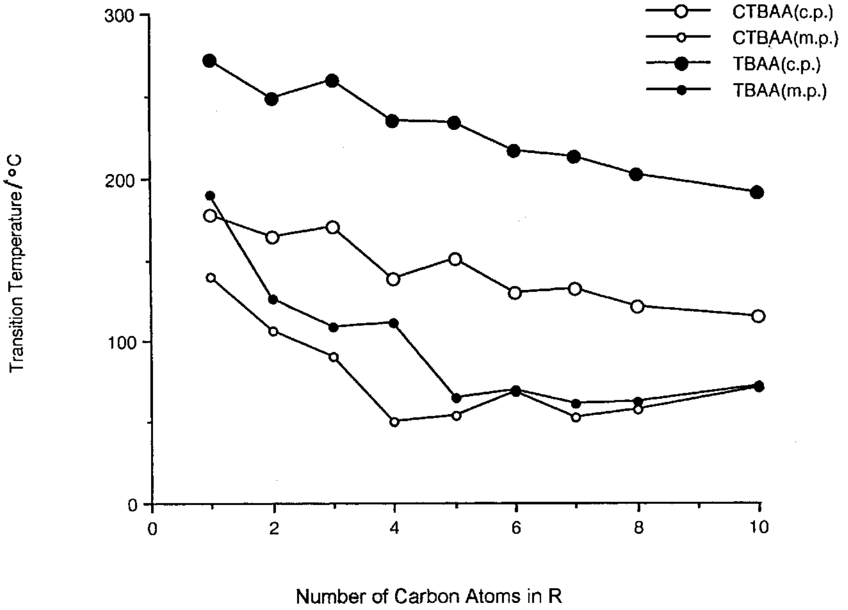
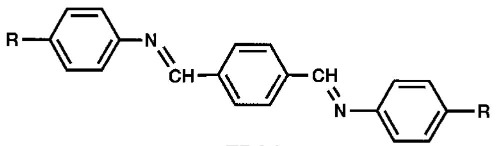


Figure 1. Transition temperatures versus alkyl chain length for CTBAA and TBAA.

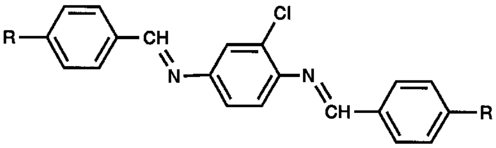
the substitution of chlorine on the central benzene ring; an 'odd–even effect' is found in the clearing temperatures. With regard to transition temperatures, the number of carbon atoms in the terminal alkyl chains has parallel effects in both series of the homologues, CTBAA and TBAA. The higher melting temperature of the TBBAs is noteworthy.

The reported crystal structure of TBBA [9] reveals an arrangement of the molecules in layers similar to that in smectic liquid crystalline phases. However, as shown in figure 2, CTBBA molecules are packed in crystals forming a staggered arrangement called an 'imbricated structure'. The chlorine substitution on the central benzene ring broadens the molecule and results in decreased intermolecular attraction; this causes the lower melting and clearing temperatures, and degradation of the layer arrangement in the crystals and the liquid crystals.

A series of 4,4′-bis-(*n*-alkylbenzal)-1,4-phenylenediamines (BAPDs), the isomers having a reversed azomethine linking group to that of TBAA, are known to show rather broad mesophases [3]. The introduction of a chlorine atom onto the central benzene ring of BAPD was effective in reducing the melting points while maintaining a broad mesophase range [10] (see the structures). The mesomorphic behaviour of CTBAAs is compared with that of 4,4′-bis-(*n*-alkylbenzal)-2-chloro-1,4-phenylenediamines (BACPDs) in figure 3. Both series of homologue exhibit almost the same transition temperatures except for the melting points of the compounds having longer alkyl chains. The orientation of the azomethine groups has only a small effect on the mesomorphic properties: it seems that the disruptive effect of the chlorine introduced onto the central benzene ring of TBAA masks the effect of the stereo structure. In order



TBAA



BACPD

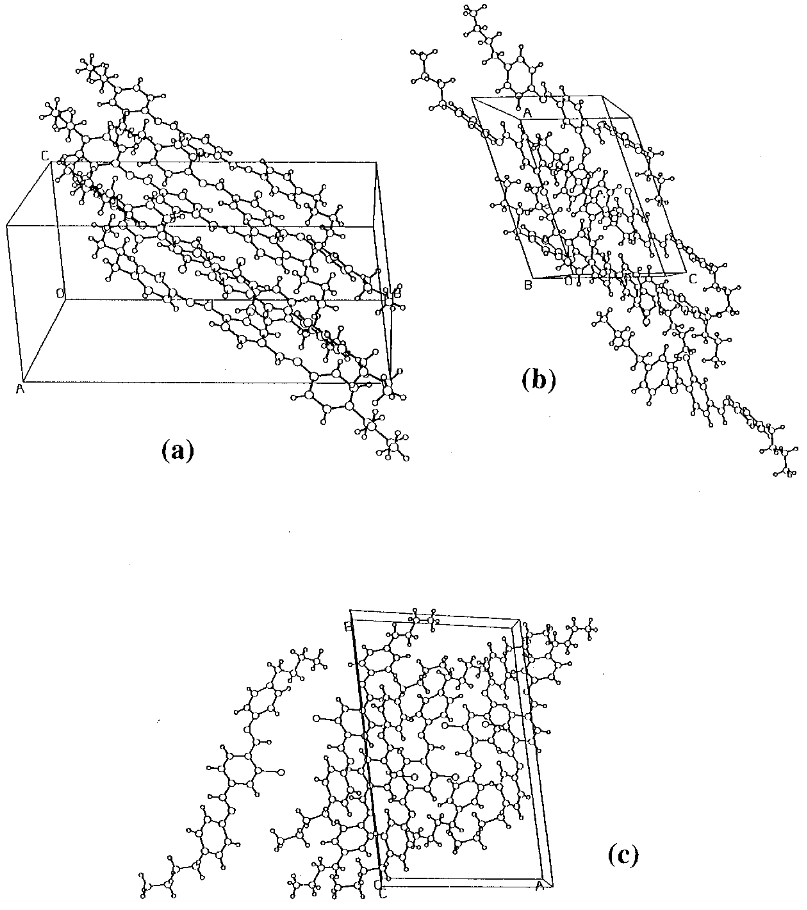


Figure 2. Schematic representation of the packing of CTBBA. (*a*) Projection along A and slightly rotated around B and C; (*b*) projection along B and slightly rotated around C and A; (*c*) projection along C and slightly rotated around A and B.

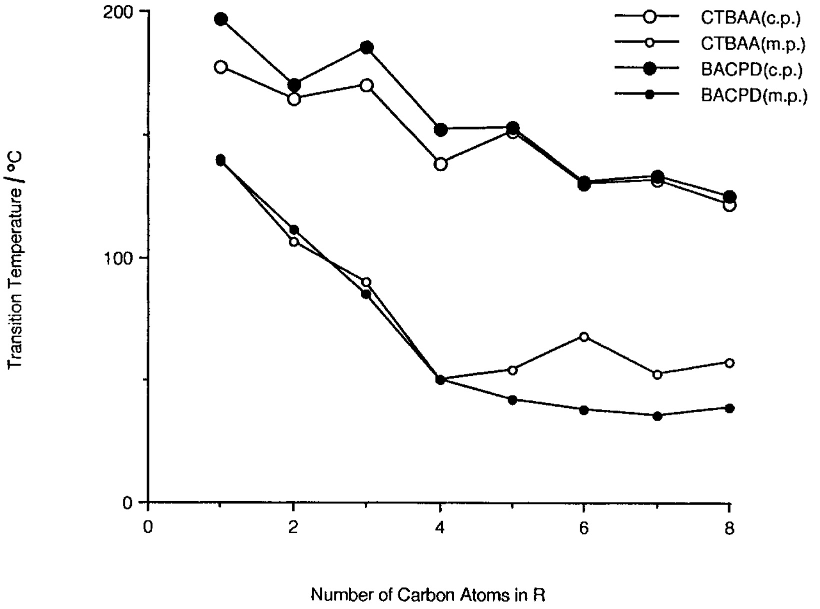


Figure 3. Transition temperatures versus alkyl chain length for CTBAA and BACPD.

to obtain information for the CTBAA, framework structure having the laterally substituted chlorine, we carried out an X-ray single crystal analysis of CTBBA as a representative compound.

There are two crystallographically different kinds of CTBBA molecule in the unit cell; their conformations are somewhat different. Atom numbering and benzene ring naming schemes are shown in figure 4. The three benzene rings, A, B and C, and D, E and F, are twisted with respect to each other. The angles of intersection between the least-squares planes of the benzene rings, A and B, and A and C, are 29° and 31°, respectively; those between D and E, and D and F, are 47° and 31°, respectively. The chlorine atom, Cl(1), the nitrogen atoms, N(1) and N(2), and the carbon atoms, C(7) and C(18), of the azomethine groups are on the least-squares plane of the central benzene ring A with mean deviation of 0·0003, 0·0099, −0·1483, −0·0348 and −0·0519 Å, respectively. Therefore, the molecules are mainly twisted at the single bonds, N(1)–C(8) and N(2)–C(19), joining the azomethine group and the side aromatic ring. In the other molecule, Cl(11), N(11), N(12), C(37) and C(48) are deviated −0·0271, 0·0277, −0·1675, −0·0450 and −0·0680 Å, respectively from the plane of the central ring D. Accordingly the laterally substituted chlorine does not sterically affect the twisted angles to such an extent. It has been reported indeed that the side benzene rings of TBBA are twisted by 16·1° and 52·9° from the central ring [7].

The final atomic parameters are given in table 2. The carbon atoms of the butyl groups have large anisotropic thermal parameters indicating their high flexibility in the

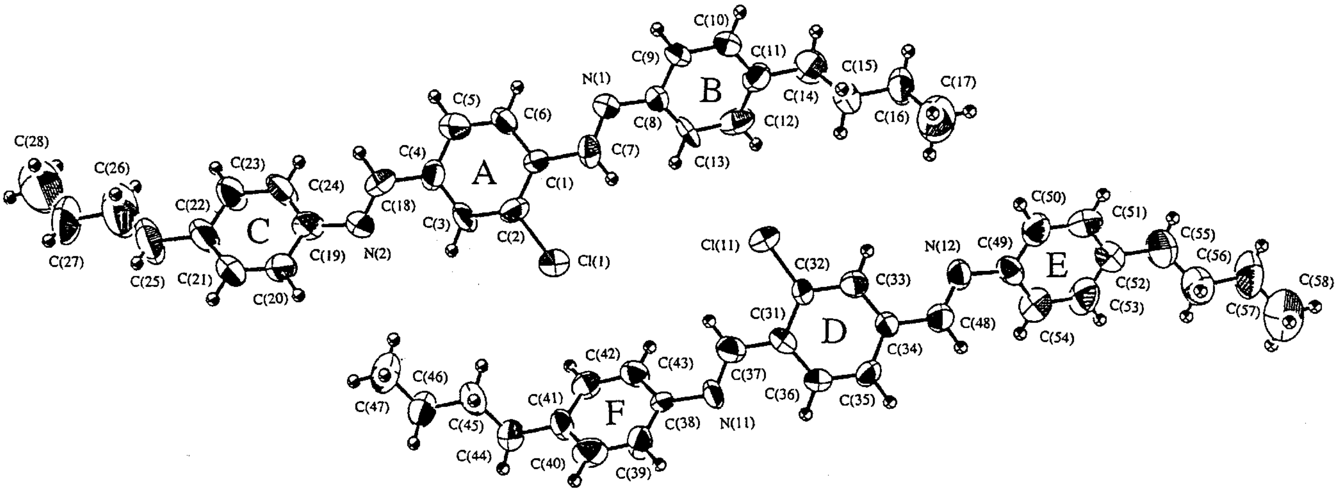


Figure 4. Molecular structures of CTBBA with numbering scheme.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$B_{eq} = (4/3)\Sigma i \Sigma j \beta ij(\mathbf{a}_i\ \mathbf{a}_j)$.

Atom	*X*	*Y*	*Z*	*B*eq
Cl(1)	1·2684(3)	0·3937(2)	0·3569(4)	6·5(2)
Cl(11)	1·4951(3)	0·6000(2)	0·1794(6)	9·1(2)
N(1)	1·0972(8)	0·5511(6)	0·200(1)	4·9(6)
N(2)	0·9800(9)	0·2572(6)	0·530(1)	5·1(6)
N(11)	1·6650(8)	0·4449(5)	0·335(1)	4·5(5)
N(12)	1·7780(8)	0·7384(6)	0·005(1)	4·8(5)
C(1)	1·097(1)	0·4529(6)	0·310(1)	4·1(7)
C(2)	1·144(1)	0·3992(7)	0·368(2)	4·8(7)
C(3)	1·096(1)	0·3532(6)	0·426(2)	4·9(7)
C(4)	0·996(1)	0·3573(7)	0·432(2)	4·8(7)
C(5)	0·951(9)	0·4112(8)	0·379(2)	6·6(8)
C(6)	1·000(1)	0·4557(6)	0·320(2)	6·0(7)
C(7)	1·143(1)	0·5035(7)	0·242(2)	4·7(7)
C(8)	1·142(1)	0·5957(7)	0·131(2)	4·2(7)
C(9)	1·116(1)	0·6566(7)	0·138(2)	5·5(7)
C(10)	1·155(1)	0·7025(6)	0·066(2)	5·4(7)
C(11)	1·221(1)	0·6904(8)	−0·014(2)	5·1(8)
C(12)	1·248(1)	0·6300(9)	−0·022(2)	6·2(8)
C(13)	1·210(1)	0·5831(6)	0·051(2)	5·6(7)
C(14)	1·265(1)	0·7412(7)	−0·093(2)	6·7(8)
C(15)	1·378(1)	0·7680(7)	−0·009(2)	7·1(8)
C(16)	1·420(1)	0·8180(8)	−0·092(2)	8·0(9)
C(17)	1·532(1)	0·8413(9)	−0·010(2)	12(1)
C(18)	0·944(1)	0·3069(8)	0·491(2)	5·2(7)
C(19)	0·919(1)	0·2114(7)	0·577(2)	5·2(7)
C(20)	0·968(1)	0·1745(7)	0·686(2)	5·7(7)
C(21)	0·912(1)	0·1296(7)	0·736(2)	7·2(8)
C(22)	0·807(1)	0·1134(7)	0·674(2)	7·8(9)
C(23)	0·758(1)	0·1503(8)	0·564(2)	9(1)
C(24)	0·814(1)	0·1972(7)	0·516(2)	6·7(8)
C(25)	0·748(2)	0·061(2)	0·726(4)	20(2)
C(26)	0·666(2)	0·057(2)	0·732(4)	19(2)
C(27)	0·606(2)	−0·004(1)	0·768(4)	17(2)
C(28)	0·518(2)	−0·005(2)	0·757(4)	21(2)
C(31)	1·669(1)	0·5433(6)	0·230(1)	4·0(7)
C(32)	1·620(1)	0·5956(6)	0·180(2)	4·4(7)
C(33)	1·670(1)	0·6450(6)	0·130(2)	5·2(7)
C(34)	1·769(1)	0·6433(6)	0·123(1)	3·9(6)
C(35)	1·819(1)	0·5921(7)	0·172(1)	4·8(7)
C(36)	1·770(1)	0·5454(6)	0·226(2)	5·1(7)
C(37)	1·618(1)	0·4907(7)	0·281(2)	5·2(8)
C(38)	1·612(1)	0·3918(6)	0·370(2)	3·7(7)
C(39)	1·660(1)	0·3628(8)	0·492(2)	5·6(7)
C(40)	1·611(1)	0·3080(8)	0·525(2)	5·9(8)
C(41)	1·515(1)	0·2781(6)	0·436(2)	5·6(8)
C(42)	1·468(1)	0·3078(7)	0·308(2)	6·0(7)
C(43)	1·515(1)	0·3641(7)	0·278(2)	5·0(7)
C(44)	1·461(1)	0·2179(7)	0·464(2)	8·0(9)
C(45)	1·374(1)	0·2267(7)	0·530(2)	7·8(9)
C(46)	1·320(1)	0·1660(8)	0·553(2)	7·6(9)
C(47)	1·236(1)	0·1771(8)	0·623(2)	10(1)
C(48)	1·822(1)	0·6928(7)	0·062(2)	5·4(7)
C(49)	1·832(1)	0·7831(7)	−0·059(2)	4·6(7)
C(50)	1·812(1)	0·846(1)	−0·051(2)	6·6(8)
C(51)	1·862(1)	0·8920(7)	−0·111(2)	6·8(8)
C(52)	1·930(1)	0·8773(8)	−0·187(2)	6·6(9)
C(53)	1·950(1)	0·816(1)	−0·197(2)	7·2(9)
C(54)	1·903(1)	0·7681(7)	−0·133(2)	6·0(8)
C(55)	1·979(2)	0·9256(9)	−0·265(2)	10(1)
C(56)	2·087(1)	0·9388(8)	−0·219(2)	9(1)
C(57)	2·129(2)	0·988(1)	−0·300(2)	12(1)
C(58)	2·238(2)	0·997(1)	−0·257(3)	16(2)

crystal. The bond distances and angles are reasonable, and all the butyl groups have the *trans* conformation.

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