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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE ADDUCT FROM THE DIASTEREOISOMERIC EQUILIBRIUM MIXTURE OF RACEMIC 2-(α-PHENYL-β-NITRO)ETHYL-4-TERT-BUTYL-CYCLOHEXANONE

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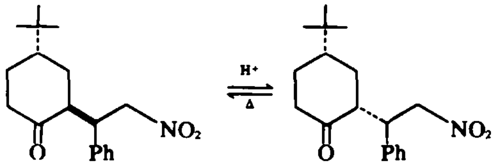
Abstract—The *trans-erythro* and *cis-threo* forms of 2 - (α - phenyl - β - nitro) - ethyl - 4 - t - butyl - cyclohexanone crystallise forming a 1:1 adduct. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions, $a = 13{\cdot}818$, $b = 22{\cdot}878$, $c = 14{\cdot}161$ Å, $\beta = 129{\cdot}6°$. The structure was determined by analysis of single-crystal diffractometry data. After refinement, based on 1523 independent reflections, the conventional R-factor was 0·088. The relative stability of the two diastereoisomers and the formation of a higher melting addition compound are discussed on the basis of structural and calorimetric data.

The *cis* of 2-alkyl-4-t-butyl-cyclohexanone usually has been considered more stable than the *trans* form,[1-4] the position of the equilibrium depending upon many factors, such as the solvent and temperature employed, and the size of the C-2 alkyl group. Recently, it has been found that *trans-erythro* 2 - (α - phenyl - β - nitro) - ethyl - 4 - t - butyl - cyclohexanone **1**, m.p. 100° epimerizes into its *cis-threo* diastereoisomer **2**, m.p. 78–79°, giving a 45:55 mixture of **1** and **2**.[5] Crystallisation of this mixture led to a compound, m.p. 114–115°, which resulted in a 1:1 adduct of **1** and **2**, by TLC and NMR. That a real compound and not a simple mixture was formed, was further confirmed by X-ray powder spectra.



1 **2**

Since the position of the equilibrium and the formation of a compound from two diastereoisomers of this type are both quite unusual, we determined the crystal structure of compound (**1**+**2**) in order to investigate its nature. Furthermore it would be possible to verify the correctness of the previous conformational and configurational assignments relative to the C_2–C_α and C_2–C_4 diastereoisomerisms.[5] Finally the structure could give some information about the influence of bulky substituents on the possible twisting or flattening of the cyclohexanone ring.

DISCUSSION

X-ray analysis shows that the crystals contain equimolar amounts of the two stereoisomers *trans* and *cis*, characterized by *erythro* and *threo* configurations respectively. Bond lengths and angles (Tables 1 and 2) in both isomers are equal within experimental errors. Unfortunately the relatively high standard deviations do not allow an accurate analysis of the eventual strains in the molecules. However the average values appear quite normal in both derivatives. In fact, the mean valency angle of "tetrahedral" carbon in the cyclohexanone ring is 111°, in agreement with recent values found in cyclohexane and cyclohexanone derivatives.[6-9] As a consequence, the average torsional angles relative to the cyclohexanic portion of the ring is lowered to 56° (Table 3). Further flattening of the chair is derived from the torsional angles around the bonds adjacent to the carbonyl group (mean 49·5°), as expected from the trigonal nature of C-1. Bond angles within the t-Bu group vary from 106° to 114°, as reported for similar compounds.[7] It may be seen from the torsional angles (Table 3) that no significant twisting of the t-Bu group occurs from its staggered conformation. This is in contrast with theoretical predictions,[10] but has already been observed.[7] The cyclohexanone ring in **1** does

Table 1. Bond distances (Å) for the two stereoisomers

Atoms	cis-threo isomer	trans-erythro isomer
O_1 - C_1	1.19(2)	1.21(2)
O_2 - N	1.18(2)	1.17(1)
O_3 - N	1.21(1)	1.21(1)
C_1 - C_2	1.53(2)	1.52(2)
C_1 - C_6	1.53(2)	1.47(1)
C_2 - C_3	1.49(2)	1.53(2)
C_2 - C_{11}	1.54(2)	1.53(2)
C_3 - C_4	1.54(2)	1.56(1)
C_4 - C_5	1.56(2)	1.53(2)
C_4 - C_7	1.50(2)	1.55(2)
C_5 - C_6	1.47(2)	1.52(2)
C_7 - C_8	1.57(3)	1.57(3)
C_7 - C_9	1.58(2)	1.57(1)
C_7 - C_{10}	1.59(2)	1.56(2)
C_{11} - C_{12}	1.52(2)	1.51(2)
C_{11} - C_{13}	1.53(2)	1.51(2)
C_{12} - N	1.52(2)	1.54(2)
C_{13} - C_{14}	1.37(2)	1.39(1)
C_{13} - C_{18}	1.39(1)	1.37(2)
C_{14} - C_{15}	1.38(2)	1.43(2)
C_{15} - C_{16}	1.34(1)	1.33(2)
C_{16} - C_{17}	1.35(3)	1.42(1)
C_{17} - C_{18}	1.40(2)	1.42(3)

[a] Standard deviations in parentheses.

Table 2. Bond angles[a] (degrees) for the two stereoisomers

Atoms	*cis*-*threo* isomer	*trans*-*erythro* isomer
$O_1 - C_1 - C_2$	123	119
$O_1 - C_1 - C_6$	123	123
$O_2 - N - O_3$	124	125
$O_2 - N - C_{12}$	117	118
$O_3 - N - C_{12}$	119	115
$C_1 - C_2 - C_3$	110	108
$C_1 - C_2 - C_{11}$	107	109
$C_1 - C_6 - C_5$	113	112
$C_2 - C_3 - C_4$	115	113
$C_2 - C_{11} - C_{12}$	110	108
$C_2 - C_{11} - C_{13}$	110	111
$C_3 - C_4 - C_5$	106	108
$C_3 - C_4 - C_7$	116	113
$C_4 - C_5 - C_6$	112	112
$C_4 - C_7 - C_8$	108	111
$C_4 - C_7 - C_9$	109	109
$C_4 - C_7 - C_{10}$	112	114
$C_8 - C_7 - C_9$	109	106
$C_8 - C_7 - C_{10}$	108	107
$C_9 - C_7 - C_{10}$	111	110
$C_{11} - C_{12} - N$	112	112
$C_{11} - C_{13} - C_{14}$	122	122
$C_{11} - C_{13} - C_{18}$	117	118
$C_{13} - C_{14} - C_{15}$	119	120
$C_{13} - C_{18} - C_{17}$	118	119
$C_{14} - C_{15} - C_{16}$	122	120
$C_{15} - C_{16} - C_{17}$	119	121
$C_{16} - C_{17} - C_{18}$	122	120

[a] Estimated standard deviation for all values is 1°.

Table 3. Torsional angles (degrees) in the two diastereoisomers

Atoms	*cis*-*threo* isomer	*trans*-*erythro* isomer
$C_1 - C_2 - C_3 - C_4$	- 56	55
$C_2 - C_3 - C_4 - C_5$	59	- 60
$C_2 - C_{11} - C_{12} - N$	-176	175
$C_3 - C_2 - C_{11} - C_{12}$	56	176
$C_3 - C_2 - C_{11} - C_{13}$	- 55	- 71
$C_3 - C_4 - C_5 - C_6$	- 57	57
$C_4 - C_5 - C_6 - C_1$	54	- 52
$C_5 - C_6 - C_1 - C_2$	- 49	50
$C_5 - C_4 - C_7 - C_8$	177	-178
$C_5 - C_4 - C_7 - C_9$	- 59	62
$C_5 - C_4 - C_7 - C_{10}$	64	- 61

not seem to be affected by the presence of a bulky axial substituent at C-2, since no significant flattening has been found, compared with 2. Finally it may be seen from Fig. 1 that in the *trans* derivative the β-carbon atom of the nitro-ethyl side chain is *anti* with respect to C-3 (torsional angle C_3–C_2–C_{11}–C_{12}, 176°), whereas in the *cis* isomer it is almost in a *gauche* conformation (torsional angle 56°). On the other hand the torsional angles around the C_2–C_{11} bond involving the phenyl ring, that is C_3–C_2–C_{11}–C_{13}, are 71° and 55° in the *cis* and *trans* stereoisomers respectively.

The molecules in the crystal are arranged in such a way as to form rows of alternate *cis* and *trans* isomers running along the [100] and [010] directions (Fig. 2a). Furthermore alternate stereoisomers proceed along a "wavy path" in the [001] direction (Fig. 2b). Since molecules are only loosely bound along the *b* axis, the crystal packing may be described in terms of "corrugated" layers, parallel to the [010] plane, whose centres are 1/2 *b* apart. It is worth noting that all the C-2 atoms maintain their configuration, e.g. R, along the [100] and [010] directions, whereas it alternates from R to S along the [001] direction. The

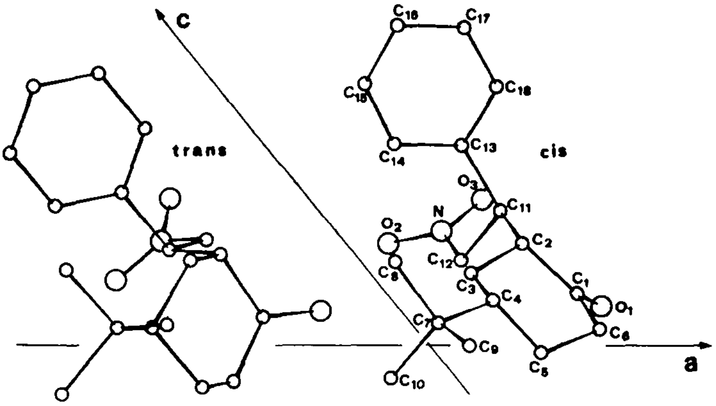


Fig. 1. A view of the two diastereoisomers along the *b* axis. The numbering scheme of the atoms is the same for both molecules.

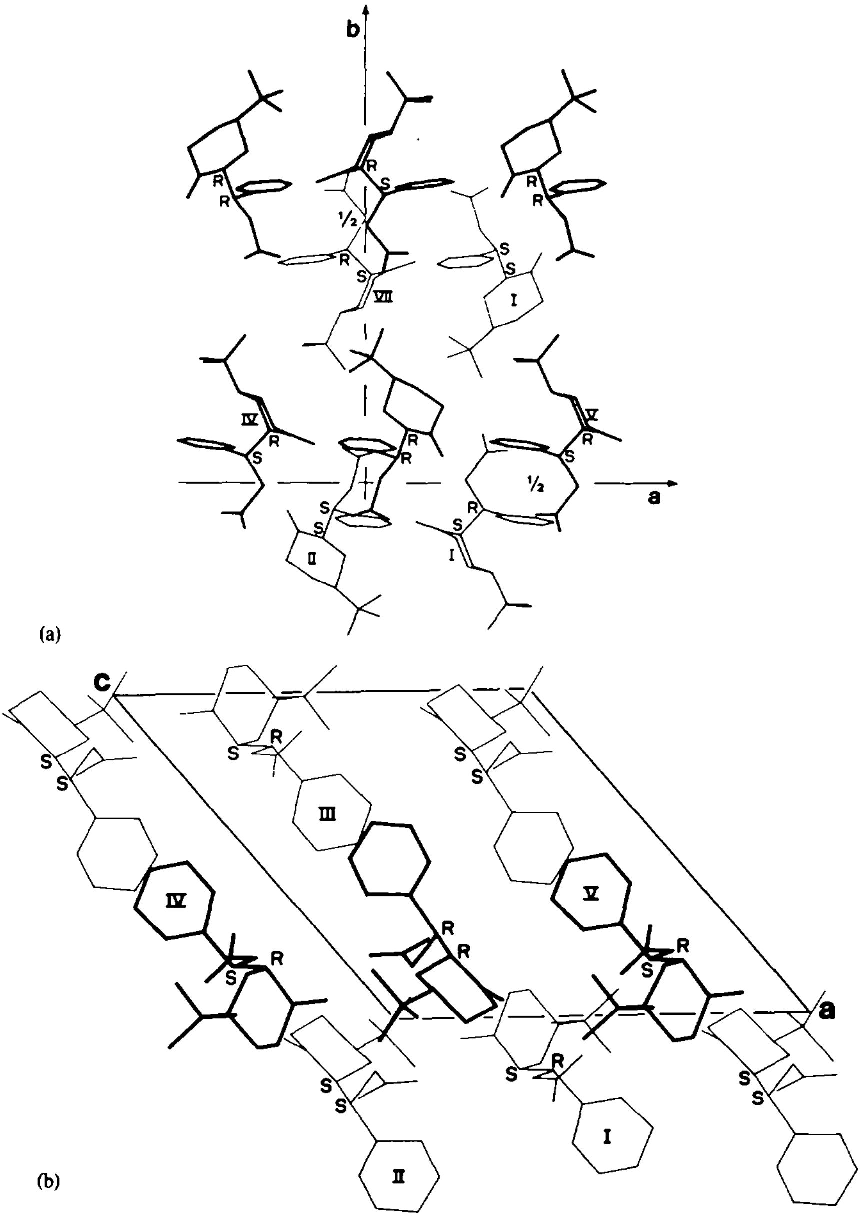


Fig. 2. Projection of the cell contents onto the (001) (a) and (010) (b) planes. The relative configuration of the asymmetric carbon atoms C-2 and C-11 is also reported. For the roman numerals see footnote in the Table 4.

contrary occurs for C-11. It seems likely that the formation in the solid state of an adduct from the racemic products **1** and **2** is just related to the possibility of obtaining the regular distribution described above. Thus the resulting crystal packing should be more efficient than in the case of the separate racemic stereoisomers, in which only interactions among isomers with the same geometric configuration are possible. This hypothesis is supported by the melting enthalpies (Table 5). It may be seen that the stereoisomers **1** and **2** have, within experimental error, the same ΔH_m (mean 6·2 kcal mol^{-1}) which in turn, is significantly lower than that of compound (**1**+**2**). However the difference is small, as expected from the nature of the intermolecular interactions and the values of the non-bonded distances, which do not allow very close packing (Table 4). This is also in agreement with the relatively high thermal factors (Table 7).

The difference in the melting points of the two stereoisomers is related to the different entropy contributions in the fusion process. In fact a greater increase in the rotational entropy of the (α-phenyl-β-nitro)ethyl group is to be expected in the case of the *cis* isomer than in that of the slightly more hindered *trans* isomer. Thus, the greater conformational contribution to ΔS_m would facilitate fusion of the *cis* compound, lowering its melting point. In compound (**1**+**2**) fusion would be even more favoured by entropy effects because of the greater number of species present in the solid, but such effects are overcome by the higher lattice energy.

Table 4. Intermolecular distances below 4Å

Distances between *cis-trans* couples

$C_8 - O_3$	3.87(2)	$C_{15} - O_2^{III}$	3.67(2)
$C_9 - O_3$	3.51(2)	$C_{15} - C_{15}^{III}$	3.72(2)
$C_1 - O_1^{I}$	3.39(1)	$C_{15} - C_{16}^{III}$	3.70(2)
$O_1 - C_2^{I}$	3.61(2)	$C_{16} - O_3^{III}$	3.87(2)
$O_1 - N^{I}$	3.55(2)	$C_{16} - C_2^{III}$	3.52(2)
$O_1 - C_1^{I}$	3.47(2)	$C_{16} - N^{III}$	3.88(2)
$O_1 - C_6^{I}$	3.50(2)	$C_{16} - C_{16}^{III}$	3.92(2)
$C_1 - C_{11}^{I}$	3.99(2)	$C_{16} - C_{17}^{III}$	3.78(2)
$O_1 - C_{12}^{I}$	3.27(2)	$C_{17} - C_{17}^{III}$	3.86(2)
$O_3 - O_1^{I}$	3.85(1)	$O_2 - O_1^{IV}$	3.75(1)
$O_3 - C_2^{I}$	3.72(2)	$O_2 - C_{12}^{IV}$	3.90(2)
$N - O_1^{I}$	3.64(2)	$C_3 - O_1^{IV}$	3.43(2)
$C_8 - C_2^{I}$	3.95(2)	$C_{10} - O_1^{IV}$	3.78(2)
$C_6 - O_3^{I}$	3.97(2)	$C_{12} - C_1^{IV}$	3.35(2)
$C_4 - N^{I}$	3.80(2)	$C_{14} - O_1^{IV}$	3.67(1)
$C_{12} - O_1^{I}$	3.49(2)	$O_1 - C_{17}^{V}$	3.66(1)
$C_3 - C_{16}^{III}$	3.49(2)	$O_1 - C_{18}^{V}$	3.51(1)
$O_2 - C_{15}^{III}$	3.78(2)	$C_1 - C_{17}^{V}$	3.74(2)
$O_2 - C_{14}^{III}$	3.73(2)	$C_1 - C_{18}^{V}$	3.83(2)
$N - C_{16}^{III}$	3.77(2)	$C_8 - C_8^{V}$	3.92(2)
$C_{14} - C_{15}^{III}$	3.91(2)	$O_3 - C_{18}^{VIII}$	3.80(2)
$C_{14} - C_{16}^{III}$	3.76(2)		

Distances between *cis-cis* couples

$C_9 - C_{15}^{I}$	3.62(3)
$O_1 - O_2^{II}$	3.87(1)
$O_3 - C_{10}^{II}$	3.91(2)
$C_2 - C_1^{II}$	3.77(1)
$O_2 - C_6^{II}$	3.97(2)
$O_2 - C_5^{II}$	3.58(2)
$O_2 - C_3^{II}$	3.90(2)
$O_2 - C_{10}^{II}$	3.96(2)
$O_2 - C_{12}^{II}$	3.99(1)
$C_{12} - C_{12}^{II}$	3.68(1)
$C_9 - C_{14}^{VII}$	3.82(2)

Distances between *trans-trans* couples

$C_{10} - C_{16}^{VI}$	3.61(2)
$C_{10} - C_{17}^{VI}$	3.99(3)
$C_{15} - O_3^{VII}$	3.83(2)

Roman numerals as superscripts refer to the following equivalent positions referred to molecules at $\underline{x}$, $\underline{y}$, $\underline{z}$:

I	$\underline{x}$	$\frac{1}{2}-\underline{y}$	$-\frac{1}{2}+\underline{z}$	V	$1-\underline{x}$	$-\frac{1}{2}+\underline{y}$	$\frac{1}{2}-\underline{z}$
II	$-\underline{x}$	$-\underline{y}$	$-\underline{z}$	VI	$\underline{x}$	$3/2-\underline{y}$	$\frac{1}{2}+\underline{z}$
III	$\underline{x}$	$\frac{1}{2}-\underline{y}$	$\frac{1}{2}+\underline{z}$	VII	$-\underline{x}$	$1-\underline{y}$	$-\underline{z}$
IV	$-\underline{x}$	$-\frac{1}{2}+\underline{y}$	$\frac{1}{2}-\underline{z}$	VIII	$\underline{x}$	$\underline{y}-1$	$\underline{z}$

Table 5. Calorimetric data relative to the two diastereoisomers and their adduct

Compound	T_m °K	$\Delta H°_m$ Kcal/mole	ΔS_m e.u.	$C_{p,c}$[(a)] cal/mole°K	$C_{p,l}$[(b)] cal/mole°K	ΔH_m at 373°K Kcal/mole
trans-erythro, **1**	373±1	6.1±0.2	16.3±0.5	115±3	30±6	6.1±0.2
cis-threo, **2**	352±1	6.3±0.2	17.9±0.5	110±3	35±6	5.6±0.3
1 + **2**	387±1	6.8±0.2	17.6±0.5	115±3	35±6	7.2±0.2

[a] Determined at about 10° below T_m.
[b] Determined at about 10° above T_m.

Table 6. Fractional coordinates (× 10⁴) for the two diastereoisomers

	cis-threo			trans-erythro		
Atoms	x	y	z	x	y	z
O1	2971(7)	471(4)	762(6)	1187(6)	5745(4)	4360(8)
O2	595(0)	-669(5)	1867(9)	3783(8)	4422(4)	3798(8)
O3	2508(7)	-756(4)	2712(7)	2019(9)	4063(5)	2305(9)
N	1523(8)	-496(5)	2092(7)	2686(9)	4425(5)	3093(8)
C1	2761(11)	938(7)	961(10)	2090(9)	5920(6)	4489(9)
C2	2571(9)	1041(6)	1902(9)	1975(9)	6019(5)	3362(8)
C3	1437(9)	1408(5)	1357(9)	2466(9)	6634(5)	3458(8)
C4	1445(10)	1999(6)	838(9)	3818(9)	6734(5)	4681(8)
C5	1557(11)	1850(6)	-166(9)	3797(11)	6644(6)	5736(10)
C6	2674(12)	1497(7)	318(10)	3301(9)	6043(6)	5693(8)
C7	395(12)	2409(6)	427(11)	4355(11)	7338(6)	4733(11)
C8	460(13)	2540(7)	1557(12)	4392(12)	7403(8)	3654(11)
C9	594(14)	3000(7)	-9(12)	5754(12)	7382(7)	5952(13)
C10	-943(14)	2140(7)	-632(13)	3593(13)	7868(7)	4642(13)
C11	2631(9)	463(5)	2501(8)	2656(8)	5524(5)	3268(7)
C12	1469(9)	99(5)	1577(8)	1992(10)	4956(6)	3080(9)
C13	2851(9)	588(5)	3687(8)	2643(9)	5623(5)	2203(8)
C14	1885(9)	647(6)	3717(9)	1524(9)	5669(5)	1001(8)
C15	2155(11)	787(6)	4812(10)	1558(12)	5772(7)	27(10)
C16	3334(10)	866(7)	5845(9)	2650(11)	5813(6)	263(9)
C17	4294(12)	807(6)	5825(10)	3797(11)	5752(7)	1479(11)
C18	4087(9)	661(6)	4748(8)	3775(10)	5667(6)	2455(10)
H2	3355	1313	2640	961	6005	2547
1-H3	1335	1486	2042	1840	6957	3392
2-H3	631	1159	594	2452	6699	2680
H4	2318	2217	1592	4439	6392	4752
1-H5	1591	2254	-562	3186	6973	5674
2-H5	719	1600	-916	4748	6697	6617
1-H6	3507	1765	987	3207	6015	6403
2-H6	2682	1375	-419	3994	5714	5896
H11	3458	216	2752	3640	5490	4121
1-H12	645	336	1303	1900	4911	3794
2-H12	1392	33	755	1022	4980	2183
H14	914	585	2886	614	5622	786
H15	1381	818	4852	712	5832	-923
H16	3540	987	6699	2657	5894	-484
H17	5263	871	6677	4696	5760	1631
H18	4870	615	4737	4644	5641	3408

[a] Standard deviations in parenthesis.

As to the composition of the mixture of **1** and **2** at equilibrium, no particular interaction within each molecule has been found which could be responsible for their relative stability. Therefore the equilibrium position should be mainly determined by a balance of the following factors: (a) the two 1,3-diaxial interactions between the (α-phenyl-β-nitro)ethyl group and the hydrogens of the ring in **1**, (b) the "2-alkylketone" effect in **2**, which tends to destabilize the equatorial position and (c) the configuration of the group at C_2, which is *erythro* in **1** and *threo* in **2**. Although the *threo* form is generally accepted to be less stable than the *erythro* one in acyclic compounds, this could also be true for cyclic ones. The *erythro* form of 2-(α-phenyl-β-nitro)ethyl-cyclohexanone in fact has been found[5] to be more stable than the *threo* form. This could be valid also in the present case, although the conformation of the group is not the same in **1** and **2**.

EXPERIMENTAL

Compounds have been prepared following the procedure indicated in ref 5. The enthalpies of melting ΔH_m at T_m were determined using a differential scanning calorimeter Perkin-Elmer, model 1B. Molar heat capacities, both of the crystals ($C_{p,c}$) and the liquid ($C_{p,l}$) were determined with the aid of the same instrument, using a sapphire disc as standard sample. The $\Delta C_p = C_{p,l} - C_{p,c}$ values so obtained were used to evaluate the enthalpies of melting of the three samples at a common temperature (373°K), and considered constant over the temperature range considered in the integral:

$$\Delta H_m = \Delta H^\circ_m - \int_{T_m}^{373°K} \Delta c_p dT = \Delta H^\circ_m - \Delta C_p(373 - T_m)$$

Crystals are monoclinic, space group $P2_1/c$ with cell dimensions, $a = 13{\cdot}818$, $b = 22{\cdot}878$, $c = 14{\cdot}161$ Å, $\beta = 129{\cdot}6°$, as determined from Weissenberg photographs (CoK_α), and refined with an on-line automated Siemens diffractometer (MoK_α, $\lambda = 0{\cdot}7107$). The calculated density of 1·17 g cm^{-3} is in agreement with the measured density of 1·16 g cm^{-3}, assuming eight formula units ($C_{18}H_{25}NO_3$) per unit cell. Three dimensional intensity data were recorded on a Siemens diffractometer by the θ–2θ scan technique with MoK_α radiation for a maximum 2θ angle of 50°. All reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for the Lorentz and polarization factors. A total of 1523 independent reflections were collected. No correction for absorption (μ = 0·09 cm^{-1}) or extinction was applied. The structure was determined by direct methods using the Multan program.[11] The E-map based on

Table 7. Anisotropic temperature factors (× 10^4) for the two diastereoisomers.[a]

	cis-threo						trans-erythro					
Atoms	B11	B12	B13	B22	B23	B33	B11	B12	B13	B22	B23	B33
O1	219(7)	-6(7)	305(7)	36(2)	-18(6)	150(5)	154(6)	-1(7)	178(7)	29(2)	-2(6)	113(5)
O2	221(-0)	-45(8)	299(11)	32(3)	-5(9)	237(9)	234(8)	30(8)	310(11)	25(2)	11(8)	221(8)
O3	195(7)	26(8)	195(9)	32(3)	18(7)	128(6)	300(10)	-51(10)	390(11)	43(3)	-101(9)	262(8)
N	130(8)	-23(9)	138(10)	28(3)	-38(8)	95(7)	199(9)	-43(9)	210(10)	25(3)	-17(8)	125(7)
C1	151(11)	-32(11)	164(13)	32(4)	-36(11)	112(9)	113(9)	17(10)	111(11)	26(3)	4(9)	73(8)
C2	141(9)	-21(9)	152(10)	23(3)	-13(8)	84(7)	125(8)	-4(9)	126(9)	17(3)	-7(8)	71(7)
C3	135(9)	4(8)	159(11)	19(3)	23(8)	102(8)	128(9)	1(9)	142(11)	15(3)	-1(8)	90(7)
C4	146(10)	-26(10)	166(12)	22(3)	1(9)	99(8)	112(8)	-3(8)	100(10)	18(3)	-7(8)	63(7)
C5	207(11)	-9(11)	193(13)	29(4)	9(10)	97(9)	170(11)	-13(11)	157(12)	26(3)	-25(10)	89(8)
C6	288(12)	-42(12)	413(11)	37(4)	-11(10)	186(8)	150(9)	-8(10)	151(10)	32(4)	-2(9)	70(6)
C7	179(13)	26(12)	107(17)	24(3)	37(11)	103(11)	147(11)	0(11)	153(14)	21(3)	-2(11)	132(10)
C8	281(13)	54(13)	411(15)	30(4)	35(12)	236(11)	212(12)	-14(13)	266(13)	36(5)	21(12)	169(10)
C9	311(16)	17(13)	367(18)	19(3)	63(11)	225(13)	118(13)	-43(13)	143(18)	36(4)	-36(13)	177(13)
C10	133(16)	-4(15)	56(23)	40(5)	37(15)	156(15)	253(15)	47(12)	347(18)	21(4)	-3(12)	249(14)
C11	139(8)	-25(9)	144(9)	17(3)	-10(7)	71(6)	152(7)	3(8)	181(8)	12(2)	5(7)	80(6)
C12	142(9)	-21(8)	117(10)	15(3)	-2(7)	65(7)	183(10)	22(9)	235(10)	19(3)	3(8)	122(7)
C13	127(8)	3(8)	120(9)	10(2)	-0(7)	71(6)	139(9)	-3(9)	148(10)	12(3)	-12(8)	89(7)
C14	141(9)	12(9)	119(10)	20(3)	-11(9)	76(8)	157(8)	-7(9)	176(10)	18(3)	-5(8)	87(7)
C15	142(11)	5(11)	116(13)	31(4)	-10(10)	81(8)	214(12)	4(12)	164(13)	30(4)	6(11)	80(9)
C16	215(10)	1(11)	236(10)	30(4)	-5(9)	113(7)	244(11)	-46(11)	257(11)	30(4)	-22(10)	110(8)
C17	174(12)	-13(12)	124(14)	36(4)	-3(10)	65(9)	213(10)	-33(12)	321(12)	38(4)	-16(11)	186(9)
C18	145(9)	-11(10)	101(10)	26(3)	-16(9)	60(7)	166(9)	-20(10)	210(11)	26(3)	-13(10)	140(8)

[a] Temperature factors are of the form exp $[-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$.

[b] Standard deviations in parentheses.

the phases obtained for the 330 reflections with $|E| > 1{\cdot}70$ revealed all 44 crystallographically independent non-hydrogen atoms. After anisotropic block-diagonal matrix least-squares refinement, the R value was 0·10.

The estimated positions of the hydrogen atoms were all in regions of positive electron density of the calculated difference Fourier synthesis. However no attempt was made to locate the hydrogens of the methyl groups in view of their higher thermal factors. The non-methyl hydrogen atoms were then included at the calculated positions and were not allowed to vary ($B = 6Å^2$) in the subsequent final refinement which reduced R to 0·088. Final atomic parameters are listed in Tables 6 and 7 with their estimated standard deviations. Atomic scattering factors were calculated by known methods.[12]

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