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(2*S*,3*S*)-2,3-Diphenyl-3-hexanecarbonitrile (α,β-Diphenyl-α-*n*-propyl-β-methylpropionitrile) (DPCN)

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Abstract. $[CH_3CH(C_6H_5)C(C_6H_5)(CN)CH_2CH_2CH_3]$, $C_{19}H_{21}N$, triclinic, colorless, m.p. 366 K, $P\bar{1}$, $a = 14{\cdot}037$ (3), $b = 6{\cdot}702$ (2), $c = 8{\cdot}796$ (2) Å, $\alpha = 104{\cdot}92$ (3), $\beta = 100{\cdot}27$ (4), $\gamma = 88{\cdot}32$ (4)°, $Z = 2$, $D_m = 1{\cdot}06$ (5) (determined by flotation in aqueous NaBr), $D_x = 1{\cdot}112$ Mg m^{-3}, $M_r = 263{\cdot}39$, $R = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2} = 0{\cdot}039$. The crystal is a racemic mixture of the (2*S*,3*S*) isomer with normal aliphatic C—C distances. The main six-carbon-atom chain has a *gauche,trans,trans* conformation; the two phenyl groups are in the *gauche* conformation.

Introduction. 5413 reflections were measured [the full sphere up to $(\sin\theta/\lambda)_{max} \le 0{\cdot}54$ Å^{-1}] using graphite-monochromatized Mo K ($\lambda = 0{\cdot}70926$ Å) radiation with an automated FACS-1 diffractometer yielding 2073 independent reflections ($1697 > 3\sigma_{F^2}$). A stepped θ–2θ-scan data-collection method was used (Baenziger, Foster, Howells, Howells, Vander Valk & Burton, 1977) with a step size ranging from 0·11 to 0·15° and background was measured at ±1·5° 2θ offset. The data were not corrected for absorption since $\mu = 0{\cdot}0692$ mm^{-1} and the crystal dimensions between parallel crystal faces were (in mm): {100}, 0·158; {010}, 0·416; {001}, 0·148. The maximum and minimum absorption corrections were expected to range only from 0·97 to 0·99. The structure was found by use of *MULTAN* (Germain, Main & Woolfson, 1971) and was subsequently refined by electron density and full-matrix least-squares methods. By using a model with 220 parameters (anisotropic temperature factors on all atoms except H, isotropic temperature factors for all H atoms, fixed H-atom positions for the phenyl and methylene H atoms but variable positions for the methyl H atoms) minimizing $R_D = \sum w(\Delta F)^2$ gave $(R_D/\sum wF_o^2)^{1/2} = 0{\cdot}039$. $R = \sum \Delta F/\sum F_o = 0{\cdot}056$ for observed reflections; the standard deviation in an observation of unit weight = 2·1. Scattering factors for C and N were taken from *International Tables for X-ray Crystallography* (1962) and those for H from Stewart, Davidson & Simpson (1965). The weight, w, is $1/S_F^2$, where S_F is the larger of two estimates of the

Table 1. *Atom parameters for* (2*S*,3*S*)-2,3-*diphenyl*-3-*hexanecarbonitrile*

	x	y	z		x	y	z
C(1)	0·9423 (2)	0·8609 (6)	0·2569 (5)	H(11)	0·956 (2)	0·842 (4)	0·363 (3)
C(2)	0·8378 (2)	0·7953 (4)	0·1806 (3)	H(12)	0·953 (2)	0·003 (4)	0·273 (3)
C(3)	0·8091 (2)	0·8341 (3)	0·0114 (3)	H(13)	0·989	0·779 (4)	0·192 (3)
C(4)	0·8731 (2)	0·7078 (4)	−0·1026 (3)	H(21)	0·832	0·653	0·173
C(5)	0·8501 (2)	0·7286 (4)	−0·2715 (3)	H(41)	0·939	0·751	−0·059
C(6)	0·9118 (3)	0·5928 (6)	−0·3788 (5)	H(42)	0·866	0·566	−0·107
C(7)	0·8284 (2)	0·0550 (4)	0·0251 (3)	H(51)	0·784	0·692	−0·315
N	0·8475 (2)	0·2223 (3)	0·0360 (3)	H(52)	0·861	0·868	−0·269
C(81)	0·7028 (2)	0·7812 (4)	−0·0574 (2)	H(61)	0·897 (2)	0·606 (4)	−0·487 (3)
C(82)	0·6695 (2)	0·5804 (4)	−0·0863 (3)	H(62)	0·980 (2)	0·629 (4)	−0·333 (3)
C(83)	0·5747 (2)	0·5250 (4)	−0·1510 (3)	H(63)	0·902 (2)	0·442 (5)	−0·373 (3)
C(84)	0·5109 (2)	0·6687 (5)	−0·1901 (3)	H(82)	0·713	0·478	−0·061
C(85)	0·5418 (2)	0·8672 (5)	−0·1629 (3)	H(83)	0·553	0·386	−0·169
C(86)	0·6372 (2)	0·9227 (4)	−0·0972 (3)	H(84)	0·445	0·630	−0·236
C(91)	0·7679 (2)	0·8852 (4)	0·2917 (3)	H(85)	0·497	0·968	−0·189
C(92)	0·7046 (2)	0·7589 (4)	0·3285 (3)	H(86)	0·658	1·062	−0·079
C(93)	0·6428 (2)	0·8360 (6)	0·4332 (4)	H(92)	0·704	0·615	0·280
C(94)	0·6430 (2)	1·0408 (6)	0·5041 (4)	H(93)	0·600	0·745	0·456
C(95)	0·7040 (3)	1·1707 (5)	0·4701 (4)	H(94)	0·601	1·094	0·577
C(96)	0·7661 (2)	1·0931 (5)	0·3647 (3)	H(95)	0·704	1·315	0·519
				H(96)	0·809	1·185	0·342

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Table 2. *Bond angles* (°) *for* (2S,3S)-2,3-*diphenyl*-3-*hexanecarbonitrile*

C(2)–C(1)–H(11)	110 (1)	C(4)–C(5)–C(6)	112·5 (2)
C(2)–C(1)–H(12)	112 (1)	C(4)–C(5)–H(51)	109
C(2)–C(1)–H(13)	111 (1)	C(4)–C(5)–H(52)	108
H(11)–C(1)–H(12)	103 (2)	C(6)–C(5)–H(51)	108
H(11)–C(1)–H(13)	109 (2)	C(6)–C(5)–H(52)	109
H(12)–C(1)–H(13)	111 (2)	H(51)–C(5)–H(52)	109
C(1)–C(2)–C(3)	112·5 (2)	C(5)–C(6)–H(61)	112 (1)
C(1)–C(2)–C(91)	111·8 (2)	C(5)–C(6)–H(62)	108 (1)
C(1)–C(2)–H(21)	107	C(5)–C(6)–H(63)	107 (1)
C(3)–C(2)–C(91)	113·6 (2)	H(61)–C(6)–H(62)	110 (2)
C(3)–C(2)–H(21)	110	H(61)–C(6)–H(63)	112 (2)
C(91)–C(2)–H(21)	101	H(62)–C(6)–H(63)	106 (2)
C(7)–C(3)–C(2)	108·2 (2)	C(2)–C(91)–C(92)	120·6 (2)
C(7)–C(3)–C(4)	106·8 (2)	C(2)–C(91)–C(96)	122·5 (2)
C(7)–C(3)–C(81)	109·9 (2)	C(92)–C(91)–C(96)	116·9 (2)
C(2)–C(3)–C(4)	110·4 (2)	C(91)–C(92)–C(93)	121·8 (2)
C(2)–C(3)–C(81)	111·5 (2)	C(91)–C(96)–C(95)	121·4 (3)
C(4)–C(3)–C(81)	110·0 (2)	C(92)–C(93)–C(94)	120·1 (3)
		C(96)–C(95)–C(94)	119·9 (3)
C(3)–C(4)–C(5)	115·2 (2)	C(93)–C(94)–C(95)	119·9 (3)
C(3)–C(4)–H(41)	109		
C(3)–C(4)–H(42)	109	C(3)–C(81)–C(82)	119·6 (2)
C(5)–C(4)–H(41)	109	C(3)–C(81)–C(86)	123·2 (2)
C(5)–C(4)–H(42)	107	C(82)–C(81)–C(86)	117·1 (2)
H(41)–C(4)–H(42)	109	C(81)–C(82)–C(83)	121·6 (2)
		C(81)–C(86)–C(85)	121·4 (2)
C(2)–C(7)–N	177 (2)	C(82)–C(83)–C(84)	120·0 (2)
		C(86)–C(85)–C(84)	120·3 (2)
		C(83)–C(84)–C(85)	119·5 (3)

standard deviation of F_{ave} propagated from counting statistics or from the scatter in agreement among equivalent reflections. Atomic positions are given in Table 1.* Bond angles are given in Table 2.

Discussion. The structure of DPCN was investigated because it is one of a series of substituted ethanes whose NMR spectra have been measured and interpreted (Wawzonek, Smolin & Durham, 1974). Some of the substituted ethanes exist in *erythro* and *threo* forms. For DPCN the two forms could not be distinguished unambiguously from the NMR spectrum, though for the series it was finally assumed that the isomer which melted at 366 K was the *erythro* [(2R,3S) or (2S,3R)] form. The structure determination reported here shows unambiguously that the crystal in reality is a racemic mixture of the *threo* [(2S,3S) and (2R,3R)] forms. Fig. 1 shows the labeling of the atoms, the bond distances, and the configuration of the molecule. The bond distances have not been corrected for thermal motion.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34611 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecule shows a number of structural features deserving special comment. The C–C distances observed range from 1·556 (3) Å for the C(2)–C(3) bond near the center of the molecule to 1·505 (4) and 1·508 (5) Å at the periphery. Fitting **T**, **L**, and **S** parameters to describe the individual atom vibration ellipsoids in terms of a rigid molecule having translational, librational and screw motions (Schomaker & Trueblood, 1968) gave the following values (all × 10^4): T (11, 22, 33, 12, 13, 23): 484 (21), 383 (26), 504 (18), 37 (20), −29 (16), −27 (18) Å^2; L (11, 22, 33, 12, 13, 23): 27 (5), 19 (2), 40 (5), 5 (2), 1 (3), −10 (3) rad^2; and S (12, 13, 21, 23, 31, 33, 11–22, 11–33): −15 (4), 18 (6), 14 (4), 7 (4), −9 (6), −18 (5), 19 (7), −11 (10) Å rad. The values indicate that translational motion parallel to the axes dominates, followed by librations about the axes, and negligible screw motions. Correcting the interatomic distances on the assumption of this rigid molecule adds 0·003 Å to the distances near the center of the molecule and up to 0·005 Å to the distances at the periphery. The observed shortening for C(4)–C(5) and C(5)–C(6) is then only partly explained.

A survey of CH_2–CH_2 distances in crystal structures reported with R values less than 0·10 indicates an average (uncorrected for thermal motion) of 1·518 [12] Å based on 126 distances. {The value in square brackets represents the scatter of values from the mean: $[\sum (x_i - \bar{x})^2/(n-1)]^{1/2}$.} Coupled with the shortened CH_2–CH_2 bond, the C–C–C bond angle is observed to be significantly larger than the idealized 109·5°: 113·6 [1·1]°. Jensen & Mabis (1966) used the relation $-\delta l = (\delta\Phi)(l)(\cos\Phi/2)/(\sin\Phi/2)(57{\cdot}3)$ to explain the bond shortening assuming that the relative thermal motion between segments along a long floppy chain gave rise to the apparently larger C–C–C angle and the consequent bond shortening. The bond angles in the

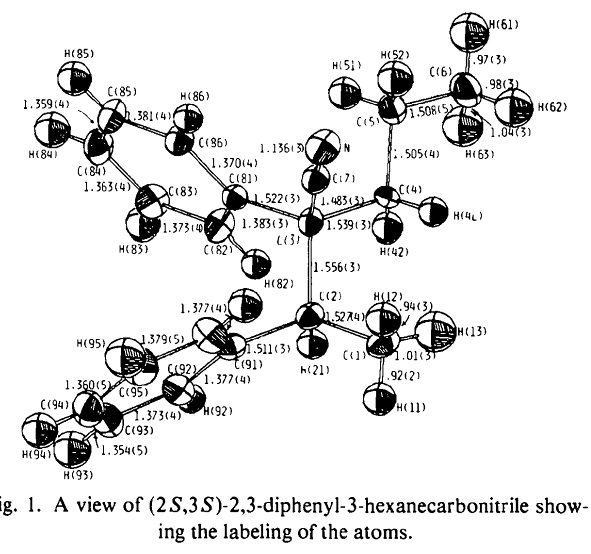

Fig. 1. A view of (2S,3S)-2,3-diphenyl-3-hexanecarbonitrile showing the labeling of the atoms.

title compound average 112·7 [2·0]°. The correction, $-\delta l = 0.018\delta\Phi$, would require a $\delta\Phi$ of 1·9° to yield a C—C distance of 1·54 Å, and thus a corrected C—C—C angle of 110·8°. (Applying this same correction to the averaged literature values gives an average angle of 112·4° to correspond to correcting the average observed distance to 1·540 Å.)

Perhaps the best comparison is between the title compound and (±)-hexestrol (Weeks, Pokrywiecki & Duax, 1973) [(3*R*,4*S*)-3,4-bis(*p*-hydroxyphenyl)-hexane]. In hexestrol the central C—C bond distance is 1·553 (6) Å, the 2,3 and 4,5 C—C bond distances are 1·539 (6) and 1·535 (6) Å, and the terminal 1,2 and 5,6 C—C bond distances are 1·504 (7) and 1·512 (8) Å. The $C-C_{ar}$ distances in hexestrol are 1·522 (6) and 1·523 (6) Å as compared to 1·511 (3) and 1·522 (3) Å in the title compound. The C—C—C bond angles in hexestrol average 112·5 [1·2]° compared to 112·7° in the title compound. In both hexestrol and the title compounds the phenyl groups have adopted a *gauche* orientation rather than *trans*. The main six-carbon-atom chain can be described as *gauche,trans,trans* in the title compound compared to approximately *trans,-trans,trans* in hexestrol.

Finally, the C≡N distance [1·136 (3) Å] and the $C-C_{CN}$ distance [1·483 (3) Å] appear to lie close to the values normally found for these bond lengths.

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4-Cyano-3-hydroxy-6*H*-1,2,6-thiadiazine 1,1-Dioxide

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Abstract. $C_4H_3N_3O_3S$, M_r = 173·16, monoclinic, $P2_1/c$, a = 8·519 (1), b = 5·5024 (2), c = 14·791 (2) Å, β = 114·50 (1)°, U = 630·9 (2) Å^3, Z = 4, D_c = 1·822 Mg m^{-3}, μ(Mo $K\alpha$) = 0·462 mm^{-1}. The structure has been refined to R = 0·043 for 1331 independent reflexions. The ring presents an envelope conformation, the S atom being at the flap. The molecules are held together by hydrogen bonds.

Introduction. Crystals of the title compound were supplied by Drs Stud and Goya (Instituto de Química Médica, CSIC, Madrid). 1832 unique reflexions were collected up to θ = 30° at 295 K on a PW 1100 diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). An $\omega/2\theta$ scan technique was used. No crystal decomposition was detected. An absorption correction was performed with *ORABS* (Schwarzenbach, 1972). After Lorentz and polarization corrections, 1331 reflexions were considered observed with $I > 2\sigma(I)$ and were used in the calculations. Scattering factors for neutral atoms and anomalous-dispersion corrections for S were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Anisotropic full-matrix refinement of non-H atoms with unit weights led to R = 0·050. The H atoms were located on a difference synthesis calculated for reflexions with $\sin\theta/\lambda < 0.5$ Å^{-1}. A good weighting scheme to prevent bias on $\langle \Delta F\rangle$ *vs* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$ was $w = w_1 w_2$, where $w_1 = K/\sigma_1^2$ and $w_2 = 1/\sigma_2^2$ with $\sigma_1 = a + b|F_o|$ and $\sigma_2^2 = c + d\sin\theta/\lambda$ (coefficients given in Table 1), calculated with *PESOS* (Martínez-Ripoll & Cano, 1975). Final refinement, with isotropic temperature factors for H atoms, gave R = 0·043 and R_w =

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