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Structure of (*R*)-*N*-(1-Phenylethyl)succinamic Acid at 110 K

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Abstract. $C_{12}H_{15}NO_3$, $M_r = 221.26$, monoclinic, $P2_1$, $a = 14.3799$ (7), $b = 5.0922$ (7), $c = 16.4737$ (11) Å, $\beta = 108.717$ (4)°, $V = 1142$ (2) Å^3, $Z = 4$, $D_m = 1.278$, $D_x = 1.286$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 7.23$ cm^{-1}, $F(000) = 472$, $T = 110$ (1) K, $R = 0.035$, $wR = 0.039$ for 1895 observed reflections. The two crystallographically independent molecules differ with respect to their conformation, but have identical bond lengths and angles. The two crystallographically independent carboxylic acid groups are linked by hydrogen bonds resulting in a cyclic dimer with disordered protons, which is rarely observed in low-temperature investigations. Also, the amide groups have identical hydrogen bonds; crystallographically equivalent molecules are connected by hydrogen bonds forming infinite chains parallel to the *b* axis.

Introduction. The interactions between chiral molecules are essential elements in many biological and chemical processes, as in enantiomer separation *via* diastereoisomeric salt formation. One of the most frequently used synthetic bases for separation of the enantiomers of racemic acids is α-phenylethylamine. As the racemic modification occurs during synthesis, the α-phenylethylamine should be separated into its optically active isomers before its use as a resolving agent. The most efficient resolving agents for this purpose are the optically active *N*-(1-phenylethyl)succinamic acids (Felder & Pitre, 1971). As a first approach to gaining a better understanding of the interactions between chiral phenylethylamine entities, a structural investigation was undertaken of the amide formed from (*R*)-1-phenylethylamine and succinic acid.

Experimental. The compound was prepared by the method of Felder & Pitre (1971) using optically active (*R*)-1-phenylethylamine {m.p. 373 K; $[\alpha]_D^{20^\circ C} = 111.5°$ (*c*: 2, EtOH)}. Colourless needle-shaped crystals were obtained by recrystallization from ethyl acetate. The crystal used for data collection had dimensions 0.03 × 0.05 × 0.5 mm. D_m was measured by flotation in a mixture of bromobenzene and chlorobenzene. Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation. The crystal was cooled to about 110 K during the data collection by an Enraf–Nonius gas-flow low-temperature device. The variations of the temperature were within 1 K.

Accurate cell dimensions and the crystal-orientation matrix were determined from least-squares refinement using the setting angles of 18 reflections ($37.2 \leq \theta \leq 45.1°$). Based on an analysis of reflection profiles the ω–2θ-scan mode, scan range [$\Delta\omega = (0.8 + 0.15\tan\theta)°$] and the maximum scan time (60 s) were selected. The intensities were recorded for reflections $-18 \leq h \leq 18$, $0 \leq k \leq 6$ and $-20 \leq l \leq 20$, which correspond to θ values in the range 1–75°. Intensities of three standard reflections (011, 400, $20\bar{4}$) were recorded every 10 000 s. They displayed no systematic variations. The orientation of the crystal was checked after every 300 reflections. Data reduction included corrections for Lorentz and polarization effects but not for absorption. 5255 reflections were measured, of which symmetry-related reflections including Friedel pairs were averaged to give 2630 unique, $R_{\rm int} = 0.043$. 1895 observed reflections [$I/\sigma(I) \geq 2$] were used for structure determination and refinement. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1990). Choosing the structure configuration to be in agreement with the known *R* configuration, the structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_{\rm cs}^2|F| + 0.000625|F|^2$, where $\sigma_{\rm cs}(|F|)$ was calculated from counting statistics. The positions of the H atoms except those of the two carboxylic acid groups were shown clearly in the difference Fourier map, calcu-

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lated after a refinement with anisotropic displacement parameters for the non-H atoms. They were introduced in idealized positions with a common isotropic displacement parameter, $B = 2.0$ Å^2; their coordinates were not included in the refinement. The difference density observed in the region of the hydrogen bonds that connect the two crystallographically independent carboxylic acid groups was very diffuse. Different models, all with $B = 2.0$ Å^2 for the H atoms, were employed in the description of the H atoms of the two carboxyl groups: (*a*) two fully populated H atoms introduced at a normal distance from the O atoms with the largest C—O distances; (*b*) two fully populated H atoms placed symmetrically between O1 and O2; (*c*) four half-populated H atoms placed at a distance of 0.9 Å from the four O atoms; and (*d*) as (*c*) but with refinement of the population parameters of the partly populated H atoms. The refinements gave (*a*) $R = 0.036$, $wR = 0.040$; (*b*) $R = 0.038$, $wR = 0.042$; (*c*) $R = 0.035$, $wR = 0.039$; and (*d*) $R = 0.036$, $wR = 0.039$. Refinement (*d*) resulted in unrealistic population parameters. Based on these results, (*c*) with four half-populated H atoms was considered to be the best model, and was used in the final refinement cycles without adjusting the H-atom parameters. The final refinements included 288 parameters and the residual electron density had values between -0.26 and 0.18 e Å^{-3}. Maximum shift after the final cycle was 0.01σ; $S = 1.01$. Distances involving the H atoms were N—H 0.84–0.87, C—H 0.94–0.97 and O—H 0.89–0.90 Å.

All calculations except the structure solution were performed with the *SDP* system (Enraf–Nonius, 1985). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), including corrections for the effect of anomalous dispersion, were used as contained in the program. The final positional parameters are listed in Table 1.*

Discussion. The asymmetric unit contains two independent molecules labelled *A* and *B*. Their bond lengths and angles are listed in Table 2. A comparison between the two molecules reveals that their molecular geometries are virtually identical. However, the *ORTEP*II (Johnson, 1976) drawings in Fig. 1 reveal that though molecules *A* and *B* are both *trans* amides, they adopt very different conformations. This amide can be expected to be built from three planar entities; the phenyl group and C6, the amide group (N, C4, O3, C3) and the carboxylic acid group (C2, C1, O1, O2). Calculations of least-squares planes for these groups show that they are planar within the experimental accuracy in both molecules *A* and *B*, but their relative orientation is different. In both molecules the phenyl group and the amide group are almost perpendicular, the interplanar angle being 104 (1)° in molecule *A* and 86 (1)° in molecule *B*.

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1*A*	0.4199 (2)	0.0203 (5)	0.5256 (1)	0.0205 (6)
O2*A*	0.3438 (1)	0.3970 (5)	0.4646 (1)	0.0250 (5)
O3*A*	0.4016 (1)	0†	0.2131 (1)	0.0206 (5)
N*A*	0.4080 (2)	0.4308 (5)	0.1814 (1)	0.0163 (5)
C1*A*	0.3873 (2)	0.1822 (7)	0.4631 (2)	0.0177 (6)
C2*A*	0.4113 (2)	0.1070 (7)	0.3840 (2)	0.0186 (6)
C3*A*	0.3883 (2)	0.3213 (6)	0.3169 (2)	0.0161 (6)
C4*A*	0.4011 (2)	0.2331 (6)	0.2333 (2)	0.0153 (6)
C5*A*	0.4748 (2)	0.5877 (7)	0.0724 (2)	0.0225 (8)
C6*A*	0.4077 (2)	0.3884 (6)	0.0939 (2)	0.0160 (6)
C7*A*	0.3046 (2)	0.3993 (6)	0.0301 (2)	0.0152 (6)
C8*A*	0.2754 (2)	0.2163 (7)	−0.0364 (2)	0.0199 (8)
C9*A*	0.1821 (2)	0.2276 (7)	−0.0969 (2)	0.0238 (8)
C10*A*	0.1167 (2)	0.4220 (7)	−0.0910 (2)	0.0231 (8)
C11*A*	0.1450 (2)	0.6039 (7)	−0.0250 (2)	0.0252 (8)
C12*A*	0.2380 (2)	0.5942 (7)	0.0351 (2)	0.0213 (8)
O1*B*	0.3150 (2)	0.5461 (5)	0.6075 (1)	0.0261 (5)
O2*B*	0.3765 (2)	0.1613 (5)	0.6670 (1)	0.0280 (6)
O3*B*	0.1283 (2)	0.3331 (4)	0.6881 (1)	0.0209 (5)
N*B*	0.0783 (2)	0.7549 (5)	0.6583 (2)	0.0176 (6)
C1*B*	0.3404 (2)	0.3850 (7)	0.6704 (2)	0.0179 (6)
C2*B*	0.3286 (2)	0.4724 (7)	0.7533 (2)	0.0194 (6)
C3*B*	0.2477 (2)	0.6764 (7)	0.7425 (2)	0.0199 (8)
C4*B*	0.1467 (2)	0.5713 (7)	0.6937 (2)	0.0174 (6)
C5*B*	−0.0781 (2)	0.8879 (8)	0.5553 (2)	0.0244 (8)
C6*B*	−0.0262 (2)	0.6917 (7)	0.6252 (2)	0.0179 (6)
C7*B*	−0.0705 (2)	0.6849 (7)	0.6981 (2)	0.0176 (6)
C8*B*	−0.1357 (2)	0.4858 (7)	0.7012 (2)	0.0201 (8)
C9*B*	−0.1741 (2)	0.4737 (7)	0.7689 (2)	0.0242 (8)
C10*B*	−0.1485 (2)	0.6603 (7)	0.8330 (2)	0.0224 (8)
C11*B*	−0.0859 (2)	0.8627 (7)	0.8290 (2)	0.0216 (8)
C12*B*	−0.0468 (2)	0.8748 (7)	0.7620 (2)	0.0196 (8)

† Coordinate fixed to define origin of non-centrosymmetric structure.

The most significant difference between the two molecules is found in the relative orientation of the amide and carboxylic acid groups. In molecule *B* they are almost perpendicular with an interplanar angle of 103 (1)° in contrast to molecule *A* where the equivalent angle is 28 (1)°. This large difference in the conformation of the molecules is probably caused by intermolecular interactions in the crystal. As the molecule contains both an amide and a carboxylic acid group it is likely that hydrogen bonding involving these groups would influence the crystal packing. The hydrogen bonds observed in this structure are listed in Table 3 and shown in Fig. 2. It is remarkable that molecules *A* and *B* are involved in identical hydrogen bonds.

Both (*R*)-*N*-(1-phenylethyl)succinamic acid molecules are *trans* amides and hydrogen bonds connect molecules of the same type (*A* or *B*) related by translational symmetry along the *b* axis. This molecular packing motif of amide groups connected

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55357 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0233]

Table 2. *Bond lengths* (Å) *and bond angles* (°)

	Molecule *A*	Molecule *B*
C1—O1	1.277 (4)	1.279 (4)
C1—O2	1.264 (5)	1.261 (4)
C1—C2	1.500 (5)	1.495 (4)
C2—C3	1.512 (4)	1.527 (5)
C3—C4	1.515 (5)	1.514 (5)
C4—N	1.345 (4)	1.347 (4)
C4—O3	1.234 (4)	1.239 (4)
C6—N	1.457 (4)	1.460 (4)
C5—C6	1.519 (5)	1.527 (5)
C6—C7	1.519 (4)	1.529 (4)
C7—C8	1.396 (5)	1.393 (5)
C7—C12	1.399 (5)	1.390 (5)
C8—C9	1.392 (4)	1.396 (6)
C9—C10	1.390 (5)	1.380 (5)
C10—C11	1.387 (5)	1.384 (6)
C11—C12	1.387 (5)	1.391 (4)
O1—C1—O2	123.7 (3)	123.9 (3)
O1—C1—C2	117.0 (3)	117.5 (3)
O2—C1—C2	119.3 (3)	118.6 (3)
C1—C2—C3	113.2 (3)	113.7 (3)
C2—C3—C4	112.9 (3)	112.7 (3)
O3—C4—N	122.8 (3)	122.6 (3)
O3—C4—C3	122.9 (3)	122.1 (3)
C3—C4—N	114.3 (3)	115.3 (3)
C4—N—C(6)	122.7 (3)	122.0 (3)
C5—C6—N	109.4 (3)	109.5 (3)
C7—C6—N	111.8 (2)	110.5 (3)
C5—C6—C7	111.6 (3)	112.4 (3)
C6—C7—C8	119.9 (3)	120.0 (3)
C6—C7—C12	121.3 (3)	121.1 (3)
C8—C7—C12	118.8 (3)	118.9 (3)
C7—C8—C9	120.8 (3)	120.4 (3)
C8—C9—C10	119.9 (3)	120.3 (3)
C9—C10—C11	119.7 (3)	119.6 (3)
C10—C11—C12	120.6 (3)	120.3 (3)
C7—C12—C11	120.3 (3)	120.5 (3)

by hydrogen bonds along a 5 Å axis is one frequently found in amides, as observed by Berkovitch-Yellin & Leiserowitz (1980) in their analysis of amide structures. The geometries of the amide groups and their hydrogen bonds agree with those found in other amides.

The carboxylic acid groups of molecules *A* and *B* are connected by hydrogen bonds forming a cyclic dimer. The packing modes of carboxylic acids have earlier been investigated by Leiserowitz (1976) and Berkovitch-Yellin & Leiserowitz (1982). They found that the cyclic dimer is a common hydrogen-bond pattern of carboxylic acids. The C—O bonds of the carboxylic acid groups are similar in *A* and *B* and have values close to those found in other disordered carboxylic acid dimers (Leiserowitz, 1976). The hydrogen-bond length of 2.64 Å is identical in ordered and disordered dimers. In his analysis of the packing modes in carboxylic acids, Leiserowitz (1976) finds that disordered dimers occur in structures where the O atoms of the C—O and the C—O—H groups have identical interactions. The present structure confirms this observation, as the carboxylic acid groups are only involved in the hydrogen bonds of the cyclic dimer.

Rather few low-temperature structure determinations were available when Leiserowitz studied the carboxylic acid dimers. The investigations of Fischer, Zolliker, Meier, Ernst, Hewat Jorgensen & Rotella (1986) on terephthalic acid showed that in this structure the carboxylic acid dimer gradually changes from a disordered structure at room temperature to an ordered one at about 80 K. Feld, Lehmann, Muir & Speakman (1981) suggested a similar behaviour for benzoic acid. The double proton exchange that occurs in the dimers has been studied by Meier, Graf & Ernst (1982) by solid-state NMR measurements. In order to investigate the occurrence of disordered carboxylic acid dimers at low temperature, use was made of the Cambridge Structural Database [CSD, Version 4.6 (Allen, Kennard & Taylor, 1983)]. A search was made for carboxylic acid structures determined at a temperature less than 273 K. Of the 210 hits 38 were discarded, either because they represented a duplicate (identical structure and temperature) or because they did not contain coordinate information.

The H atoms were not included in an initial definition of the dimer which resulted in 63 carboxylic acid dimers found in 51 different structures. A similar search with the H atoms included gave 48 dimers in 39 different structures, showing that the positions of the H atoms were not determined in 15 of the cyclic carboxylic acid dimers studied at low temperature. However, this is not a sufficient indication for disorder; it should also be reflected in the C—O distances. If the carboxylic acid dimer is disordered the two C—O bonds should be similar with a bond length of *ca* 1.26 Å. An inspection of the molecular geometry of the carboxylic acid dimers revealed a difference of *ca* 0.01 Å between the

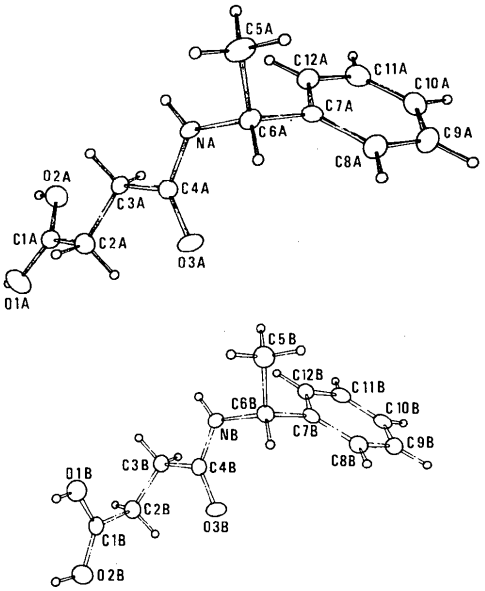

Fig. 1. *ORTEP*II (Johnson, 1976) drawings of the two crystallographically independent molecules showing the atomic numbering scheme. The thermal ellipsoids enclose 50% probability, the H atoms are drawn as spheres.

Table 3. *Hydrogen-bond geometry* (Å, °)

	Donor···Acceptor	Donor—H···Acceptor	H···Acceptor
O1B···O2A	2.631 (3)	–	–
O1A···O2B	2.638 (3)	–	–
NA—HNA···O3A^{i}	2.952 (4)	154	2.17
NB—HNB···O3B^{i}	3.034 (4)	163	2.19

Symmetry code: (i) x, $y + 1$, z.

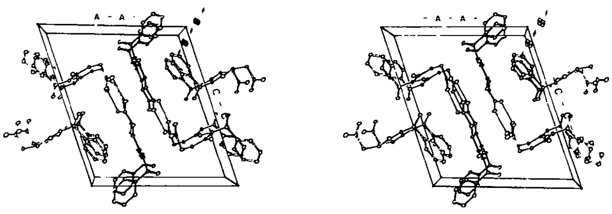

Fig. 2. A stereo pair (Johnson, 1976) seen along the b axis illustrating the molecular packing. The molecules are drawn as in Fig. 1 and the hydrogen bonds are shown as thin lines.

two C—O bonds in the carboxylic acid for two of the dimers where the H atoms were not located, 2,2-dibromo-1-methylcyclopropanecarboxylic acid (Rømming & Sydnes, 1987) and *trans*-dichlorobis-(*trans*,*trans*-dibenzylideneacetone)dioxouranium(IV) acetic acid solvate (Alcock, de Meester & Kemp, 1979), providing evidence for a disordered carboxylic acid dimer at low temperature in these two structures.

The CSD search showed that the present structure represents one of the few exceptions from the general observation that the hydrogen-bonded carboxylic acid dimers tend to be ordered at low temperature. This could indicate that disorder in (R)-N(1-phenylethyl)succinamic acid is of static origin.

Another interesting aspect of this molecule is that, though the two independent molecules are involved in identical hydrogen-bond patterns, they adopt different conformations. The non-bonded interactions between the chiral moieties will also influence the crystal packing and may contribute to the conformational differences.

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Structures of 9-Ethyl-3-nitrocarbazole and 1-(9-Carbazolyl)-3-(3-nitro-9-carbazolyl)propane

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Abstract. 9-Ethyl-3-nitrocarbazole, $C_{14}H_{12}N_2O_2$, $M_r = 240.26$, triclinic, $P\bar{1}$, $a = 10.572$ (4), $b = 12.910$ (5), $c = 9.547$ (4) Å, $\alpha = 94.85$ (3), $\beta = 111.62$ (3), $\gamma = 75.40$ (4)°, $V = 1172$ (1) Å^3, $Z = 4$, $D_m = 1.35$, $D_x = 1.361$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.869$ cm^{-1}, $F(000) = 504$, $T = 302$ K, $R = 0.061$, wR

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