

**Molecular and Crystal Structures of the α and β Forms of
2,6-Dimethyl-4-(α,α -diphenylmethylene)-1,4-benzoquinone* (2,6-Dimethylfuchson):
Evidence for the Thermal Conversion of the Racemic Crystals (1α) to the
Chiral Crystals (1β)**

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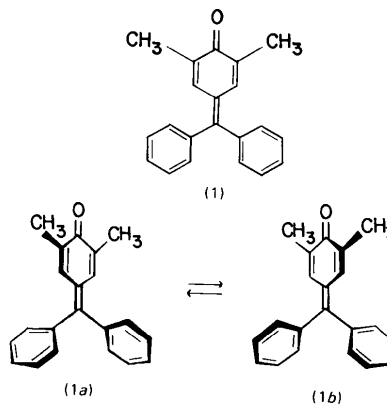
Abstract

The crystal structures of two modifications of 2,6-dimethyl-4-(α,α -diphenylmethylene)-1,4-benzoquinone (2,6-dimethylfuchson) (1) have been determined. One of the forms, (1α), belongs to the space group $P2_1/c$ with $a = 8.531$ (2), $b = 18.677$ (5), $c = 10.021$ (1) Å, $\beta = 90.87$ (2)°, $Z = 4$, and has been refined to an R factor of 0.053 on 1992 non-zero reflections. The other form, (1β), belongs to the space group $P2_12_12_1$ with $a = 8.156$ (2), $b = 17.761$ (4), $c = 10.959$ (1) Å, $Z = 4$ and has been refined to an R factor of 0.045 on 1452 non-zero reflections. The molecular structures of (1) in the forms (1α) and (1β) are almost identical, and, in the conformation found in the crystal, the molecules exhibit chirality. In both crystals, molecules of the same chirality pack in layers that are almost identical. However, the relationship between adjacent layers is different in the two forms, involving only congruent operations in the (1β) form, while enantiomorphic operations are involved in the (1α) form. Some evidence for a phase transition from the racemic (1α) to the chiral (1β) is presented. Changes are observed on powder pictures when a ground sample thought to contain (1α) and (1β) is heated to 383 K. These changes can be explained by conversion of (1α) to (1β).

Introduction

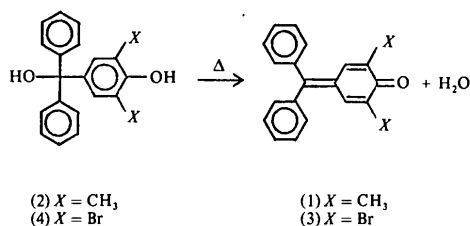
If molecules such as 2,6-dimethyl-4-(α,α -diphenylmethylene)-1,4-benzoquinone (2,6-dimethylfuchson) (1) adopted the planar arrangement in which they are often drawn, they would not exhibit chirality. However, if the rings are twisted in an asymmetric sense, the molecule becomes chiral ($1a$ and b). In fluid media,

simple rotations about bonds would result in rapid interconversions of enantiomers and thus no effects due to chirality would be observed. However, in the crystal, a molecule such as (1) can be locked into a conformation that renders the molecule chiral. In such situations, the molecules can form racemic crystals each with equal numbers of the two enantiomers, or they can form an approximately equal mixture of chiral crystals. An interesting example showing many of the above phenomena is the case of binaphthyl (Pincock & Wilson, 1971; Pincock, Perkins, Ma & Wilson, 1971).



We became interested in the crystal structure of (1) as it is the product of a solid-state dehydration of (4-hydroxy-2,5-dimethylphenyl)diphenylmethanol (2) (Lewis, Curtin & Paul, 1979). In the course of these investigations we discovered that at least three single-crystal forms of (1) could be obtained. These forms, designated (1α), (1β), and (1γ), crystallize in the space groups $P2_1/c$, $P2_12_12_1$, and $Pna2_1$, respectively. The present paper contains a description of the structures of the (1α) and (1β) forms, a comparison of their crystal packing, and evidence for a transition (1α) to (1β). The structure of (1γ) is described in a separate paper (Duesler, Lewis, Curtin & Paul, 1979).

* IUPAC name: 2,6-dimethyl-4-(diphenylmethylene)-2,5-cyclohexadienone.



Experimental

The synthesis and characterization of 2,6-dimethyl-4-(α,α -diphenylmethylene)-1,4-benzoquinone (1) was described previously (Lewis, Curtin & Paul, 1979).

Single crystals of the α form of (1) were obtained by slow evaporation of either a benzene or a cyclohexane solution. The crystals of (1 α) obtained from benzene solution were rectangular tablets; those obtained from cyclohexane were well formed hexagonal-shaped crystals with all three external dimensions of approximately the same length.

Single crystals of the β form of (1) were obtained by slow evaporation of a benzene, or cyclohexane, or toluene solution. The crystals of (1 β) obtained from benzene solution were very similar in appearance to those of (1 α) obtained from benzene. The crystals of (1 β) obtained from cyclohexane and toluene solution were very similar in appearance to those of (1 α) obtained from cyclohexane solution. All four of the crystals obtained from toluene and which were identified by X-ray methods were found to be of the (1 β) form. In general, however, the only definitive method of distinguishing between crystals of (1 α) and (1 β) was by single-crystal X-ray methods. Preliminary goniometric studies on (1 α) and (1 β) (from cyclohexane and toluene solution) showed preferred development of the following faces: (010), (110), (110), (011), (011), (011), (011), (012), (012), (012), (012). Single crystals of (1) [the distinction between (1 α) and (1 β) was not studied in this respect] were observed to show pleochromism under polarized light. The crystals appeared more yellow at one setting and more orange at a setting 90° away.

A few crystals of a different form of (1), (1 γ), were obtained along with crystals of (1 α) and (1 β) upon evaporation of a saturated cyclohexane solution. Only one crystal of this form was studied by X-ray methods, and was easily distinguished from (1 α) and (1 β) because it was a very long, thin, needle-like crystal which was taken from a large number of similar needles grown together in a cluster. Crystal data for all three forms of (1) are given in Table 1.*

* On slow evaporation of a CH₂Cl₂ solution of (1), well formed rectangular tablets were obtained, but these were not studied or identified by X-ray methods.

Structure determination of form (1 α)

Studies were carried out on a crystal of dimensions 0.3 × 0.2 × 0.1 mm obtained from cyclohexane solution. Cell dimensions (Table 1) were determined by a least-squares fit to the settings for fifteen high-order reflections (Cu K α , $\lambda = 1.54178 \text{ \AA}$).

Intensity data were collected on a Syntex P2₁ diffractometer (Cu K α ; graphite monochromator). Reflections in the range $2\theta = 2^\circ$ to 130° were measured by a 2θ scan method using a moving-crystal moving-counter technique with scan speeds ranging from 2 to $10^\circ \text{ min}^{-1}$. The background to scan time ratio used was 0.25. The intensities of three standard reflections, measured every fifty reflections, did not show any evidence of crystal decay throughout the data collection. Reflections were collected over one-quarter of the sphere and symmetry-related reflections were averaged to obtain 2709 reflections, of which 1992 (73.5%) were considered non-zero at the 1.96σ level according to counting statistics. No absorption or extinction corrections were applied.

The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F)$ is the standard deviation based on counting statistics. The atomic scattering factors used in the calculation of all structure factors were taken from the analytical expressions given in *International Tables for X-ray Crystallography* (1974).

The structure was solved using the *MULTAN* series of programs (Germain, Main & Woolfson, 1971). Least-squares refinement incorporating positional and anisotropic thermal parameters for the non-hydrogen atoms gave an *R* factor of 0.098. Positions were calculated for the ten aromatic and two olefinic H atoms and were included in the model. After one cycle of block-diagonal least-squares refinement varying positional and anisotropic thermal parameters for all

Table 1. *Crystal data for the three forms of 2,6-dimethyl-4-(α,α -diphenylmethylene)-1,4-benzoquinone (1)*

	(1 α)	(1 β)	(1 γ)*
Molecular formula	C ₂₁ H ₁₈ O	C ₂₁ H ₁₈ O	C ₂₁ H ₁₈ O
Molecular weight	286.4	286.4	286.4
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2₁/c</i>	<i>P2₁2₁2₁</i>	<i>Pna2₁</i>
<i>a</i> (Å)	8.531 (2)	8.156 (2)	11.820 (3)
<i>b</i> (Å)	18.677 (5)	17.761 (4)	16.487 (4)
<i>c</i> (Å)	10.021 (1)	10.959 (1)	8.150 (2)
β (°)	90.87 (2)		
Volume (Å ³)	1596	1588	1588
<i>Z</i>	4	4	4
<i>D</i> (calc.) (Mg m ⁻³)	1.19	1.20	1.30

* Data taken from Duesler, Lewis, Curtin & Paul (1979).

non-hydrogen atoms and positional and isotropic thermal parameters for the H atoms, a difference map was calculated from which the positions of the six methyl-group H atoms were found. Three cycles of block-diagonal least-squares refinement followed by five cycles of full-matrix least-squares refinement varying positional and anisotropic thermal parameters for all the non-hydrogen atoms and positional and isotropic thermal parameters for all H atoms converged to an R factor of 0.053 and an R_2 value, $R_2 = (\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2)^{1/2}$, of 0.055 on all non-zero reflections. The final value of $[\sum w||F_o| - |F_c||^2 / (m - n)]^{1/2}$ was 1.65. A difference map, obtained after refinement of the model was completed, contained

no electron density above $0.16 \text{ e } \text{\AA}^{-3}$. The final atomic coordinates for (1 α) are given in Table 2.*

Structure determination of (1 β)

Studies were carried out on a crystal of dimensions of $0.4 \times 0.2 \times 0.1 \text{ mm}$ obtained from toluene solution. Cell data (Table 1) were obtained as for (1 α). The details of the data collection were as described

* The final values of the thermal parameters and structure factors for (1 α) and (1 β), and Table 8 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34650 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final atomic coordinates in fractions of the unit-cell edge for (1 α)

	x	y	z
C(1)	0.0823 (2)	0.2398 (1)	0.0682 (2)
C(2)	-0.0800 (3)	0.2279 (1)	0.0178 (2)
C(3)	-0.1669 (3)	0.1689 (1)	0.0619 (3)
C(4)	-0.3175 (4)	0.1572 (2)	0.0126 (4)
C(5)	-0.3841 (4)	0.2026 (2)	-0.0807 (4)
C(6)	-0.2996 (4)	0.2597 (2)	-0.1260 (3)
C(7)	-0.1485 (3)	0.2725 (2)	-0.0780 (3)
C(8)	0.1801 (2)	0.1747 (1)	0.0868 (2)
C(9)	0.2647 (3)	0.1632 (1)	0.2051 (2)
C(10)	0.3519 (3)	0.1013 (1)	0.2232 (3)
C(11)	0.3561 (3)	0.0504 (1)	0.1236 (3)
C(12)	0.2720 (3)	0.0605 (1)	0.0065 (3)
C(13)	0.1833 (3)	0.1218 (1)	-0.0113 (3)
C(14)	0.1398 (2)	0.3071 (1)	0.0960 (2)
C(15)	0.0396 (3)	0.3682 (1)	0.1196 (2)
C(16)	0.0949 (3)	0.4339 (1)	0.1485 (2)
C(17)	0.2649 (3)	0.4469 (1)	0.1494 (2)
C(18)	0.3691 (3)	0.3863 (1)	0.1227 (2)
C(19)	0.3081 (3)	0.3205 (1)	0.1028 (2)
C(20)	-0.0112 (4)	0.4949 (2)	0.1850 (4)
C(21)	0.5425 (3)	0.4007 (2)	0.1166 (4)
O	0.3183 (2)	0.5076 (1)	0.1736 (2)
H(3)*	-0.116 (3)	0.135 (1)	0.136 (3)
H(4)	-0.375 (4)	0.115 (2)	0.053 (3)
H(5)	-0.493 (4)	0.193 (2)	-0.111 (3)
H(6)	-0.342 (4)	0.291 (2)	-0.190 (3)
H(7)	-0.090 (3)	0.315 (1)	-0.107 (2)
H(9)	0.259 (3)	0.202 (1)	0.278 (2)
H(10)	0.410 (3)	0.096 (1)	0.307 (3)
H(11)	0.423 (3)	0.006 (1)	0.138 (3)
H(12)	0.275 (3)	0.022 (1)	-0.065 (3)
H(13)	0.123 (3)	0.128 (1)	-0.094 (2)
H(15)	-0.077 (3)	0.360 (1)	0.118 (2)
H(19)	0.376 (2)	0.281 (1)	0.083 (2)
H(20a)	-0.124 (5)	0.485 (2)	0.166 (4)
H(20b)	0.018 (4)	0.538 (2)	0.140 (3)
H(20c)	0.005 (4)	0.509 (2)	0.284 (3)
H(21a)	0.605 (4)	0.355 (2)	0.101 (3)
H(21b)	0.571 (4)	0.435 (2)	0.049 (4)
H(21c)	0.590 (4)	0.418 (2)	0.196 (4)

* Hydrogen atoms are given the numbers of the atoms to which they are bonded.

Table 3. Final atomic coordinates in fractions of the unit-cell edge for (1 β)

	x	y	z
C(1)	0.5855 (3)	-0.5069 (1)	1.0302 (2)
C(2)	0.4203 (3)	-0.5139 (1)	0.9752 (2)
C(3)	0.3192 (4)	-0.5740 (2)	1.0048 (3)
C(4)	0.1640 (4)	-0.5821 (2)	0.9526 (3)
C(5)	0.1101 (4)	-0.5307 (2)	0.8688 (3)
C(6)	0.2092 (4)	-0.4702 (2)	0.8371 (3)
C(7)	0.3629 (4)	-0.4615 (2)	0.8892 (3)
C(8)	0.6766 (3)	-0.5785 (1)	1.0486 (3)
C(9)	0.7501 (4)	-0.5944 (2)	1.1606 (3)
C(10)	0.8319 (4)	-0.6628 (2)	1.1788 (3)
C(11)	0.8405 (4)	-0.7142 (2)	1.0851 (4)
C(12)	0.7672 (4)	-0.6996 (2)	0.9749 (4)
C(13)	0.6854 (4)	-0.6321 (1)	0.9563 (3)
C(14)	0.6525 (3)	-0.4388 (1)	1.0650 (2)
C(15)	0.5544 (3)	-0.3719 (1)	1.0850 (3)
C(16)	0.6177 (3)	-0.3070 (1)	1.1259 (3)
C(17)	0.7950 (3)	-0.2996 (1)	1.1441 (3)
C(18)	0.8969 (3)	-0.3656 (2)	1.1233 (3)
C(19)	0.8275 (3)	-0.4314 (2)	1.0886 (3)
C(20)	0.5112 (5)	-0.2400 (2)	1.1579 (4)
C(21)	1.0799 (4)	-0.3590 (2)	1.1415 (4)
O	0.8557 (3)	-0.2390 (1)	1.1783 (3)
H(3)*	0.358 (4)	-0.606 (2)	1.066 (3)
H(4)	0.099 (7)	-0.641 (3)	0.985 (5)
H(5)	-0.006 (5)	-0.546 (2)	0.823 (3)
H(6)	0.170 (5)	-0.433 (2)	0.774 (4)
H(7)	0.436 (4)	-0.422 (2)	0.863 (3)
H(9)	0.738 (4)	-0.558 (2)	1.230 (3)
H(10)	0.889 (4)	-0.675 (2)	1.260 (3)
H(11)	0.903 (6)	-0.762 (3)	1.097 (4)
H(12)	0.765 (4)	-0.735 (2)	0.911 (4)
H(13)	0.633 (6)	-0.618 (2)	0.883 (5)
H(15)	0.435 (4)	-0.378 (1)	1.076 (3)
H(19)	0.899 (4)	-0.467 (2)	1.070 (3)
H(20a)	0.412 (8)	-0.240 (3)	1.124 (6)
H(20b)	0.564 (5)	-0.192 (2)	1.124 (4)
H(20c)	0.507 (7)	-0.225 (3)	1.248 (6)
H(21a)	1.140 (5)	-0.412 (2)	1.123 (4)
H(21b)	1.117 (5)	-0.312 (2)	1.093 (3)
H(21c)	1.114 (7)	-0.336 (3)	1.226 (5)

* Hydrogen atoms are given the numbers of the atoms to which they are bonded.

previously. There was no evidence for crystal decomposition. Reflections were collected over one-quarter of the sphere and the Friedel pairs (assuming *mmm* symmetry) were averaged to obtain 1575 unique reflections, of which 1452 (92.2%) were considered observed at the 1.96σ level according to counting statistics. No absorption or extinction corrections were applied.

The structure was solved using the *MULTAN* programs (Germain, Main & Woolfson, 1971). Least-squares refinement incorporating positional and anisotropic thermal parameters for the non-hydrogen atoms gave an *R* factor of 0.086. The positions of the ten aromatic and two olefinic H atoms were calculated and then included in the model; after four cycles of block-diagonal least-squares refinement varying positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the H atoms, a difference map was calculated from which the positions of the six methyl-group H atoms were found. Four cycles of block-diagonal least-squares refinement and six cycles of full-matrix least-squares refinement varying positional and anisotropic thermal parameters for all non-hydrogen atoms and positional and isotropic thermal parameters for all H atoms converged to an *R* factor of 0.045 and an R_2 of 0.051. The 'goodness of fit' for the model was 1.99. A final difference map, obtained after refinement of the model was completed, had no significant electron density above $0.17 \text{ e } \text{Å}^{-3}$. The final atomic coordinates for (1 β) are given in Table 3.*

X-ray powder photographs

Powder photographs were taken with a camera made by Charles Supper Co., using Ilford type *G* film and Ni-filtered $\text{Cu } K\alpha$ ($\lambda = 1.54178 \text{ Å}$) radiation. Powder photographs were taken on a sample of (1) which was recrystallized by rapid cooling of a benzene-hexane solution and ground (picture *A*) and of the *same* sample which had been heated for 8 d at 383 K in a sealed glass capillary (picture *B*). The powder photographs were not visually identical. Theoretical powder patterns for (1 α) and (1 β) were calculated from the respective cell data using the program *DCALC* (Dieterich, 1973); the results of these calculations are shown in Table 4. These experiments were carried out on several distinct samples of (1) with reproducible results.

Control experiments were carried out to ensure that, upon heating, the microcrystalline sample of (1) remained chemically intact and did not undergo decomposition. A large sample of (1), ground and heated at 383 K for 7 d in a sealed tube, gave an NMR spectrum identical to that of an authentic sample

Table 4. *Observed and calculated powder d spacings (>5 Å) for (1)*

The reflection resulting in the calculated *d* spacing is given in parentheses.

Where the intensity of a reflection is relatively weak ($F_{\text{obs}} < 20$), the entry in the column for calculated values is in square brackets.

Picture <i>A</i>	Picture <i>B</i>	(1 α) (calc.)	(1 β) (calc.)
9.358	—	9.339 (020)	[9.327 (011)]
—	8.856	[8.830 (011)]	8.880 (020)
8.560	—	8.530 (100)	—
7.745	—	7.759 (110)	—
—	7.383	—	7.412 (110)
6.854	6.889	6.832 (021)	6.900 (021)
—	—	—	[6.543 (101)]
6.222	—	6.298 (120)	—
—	6.130	[6.094 (111)]	6.140 (111)
—	—	—	[6.007 (120)]
5.474	5.467	—	5.480 (002)
5.280	5.227	{ [5.306 (121)] [5.288 (031)]	{ [5.268 (121)] [5.236 (012)] [5.209 (031)]

of (1) and also had a melting point identical to that of the sample of (1) obtained before heating.

Although single crystals of (1 β) may be obtained with some confidence from slow evaporation of a toluene solution, single crystals of (1 α) were obtained only from solvent systems which also gave (1 β) and were not readily separable. Thus, the experiment in which single crystals of (1 α) were ground prior to obtaining an X-ray powder photograph was not conducted. However, other evidence indicated that grinding was necessary to initiate any change. Single crystals of (1 α) remained unchanged on the basis of X-ray photographs when heated under the same conditions as the microcrystalline sample discussed earlier. Even breaking one end of a single crystal of (1 α) with a needle, thus introducing severe defects at one end, did not initiate any change in (1 α) upon heating.

Experiments were conducted with the hope of finding some evidence for the intermediacy of (1 α) in the solid-state thermal dehydration of (2) to (1) [the form obtained is (1 β)] (Lewis, Curtin & Paul, 1979). Both single crystals of (2) and microcrystalline samples of (2) were heated at 383 K for lengths of time less than those necessary for the complete dehydration of (2) to occur. Powder photographs were then taken of these partially dehydrated samples. The observed powder photographs of these samples were very complex, but no evidence indicating the presence of (1 α) was found.

Results and discussion

The results of the X-ray analyses of (1 α) and (1 β) show that, while the two crystal modifications have rather similar morphology and cell dimensions, they belong to different crystal systems and have different space

* See previous footnote.

groups. While a crystal of the (1 α) form ($P2_1/c$) must contain both enantiomeric molecules, one crystal of the (1 β) form ($P2_12_1$) can contain only one of the two enantiomeric molecules.

Stereoscopic views of the molecules of (1) found in the (1 α) and (1 β) forms are shown in Fig. 1. In this figure the same enantiomer is displayed and the atom numbering is given. The molecular structures in the two crystal forms are virtually identical. Bond lengths and angles are given in Table 5. Most of these dimensions are within the range of normally accepted values. The comparable bond lengths and angles for the quinone-like portions are in reasonably good agreement with those reported for 2,6-dimethyl-1,4-benzoquinone (Rabinovich & Schmidt, 1967). In molecules of both forms, there are significant deviations from ideal geometry at the sp^2 centers at C(1) and C(14), presumably to relieve steric overcrowding of the α,α -diphenylmethylene functionality; the C(15)–C(14)–C(19) and C(2)–C(1)–C(8) angles are compressed (116.1°) with concomitant increases in the other angles at these centers. This angular distortion, combined with a lengthening of the C(1)–C(14) bond relative to the C(15)–C(16) and C(18)–C(19) bonds, places the diphenyl substituents as far away as possible from the quinone-like ring.

The unsubstituted phenyl rings in both forms are accurately planar; however, the quinone-like rings are

rather less planar, with a very similar pattern of distortions in both crystals (Table 6). The distortions found in the crystals of (1 α) and (1 β) are much less

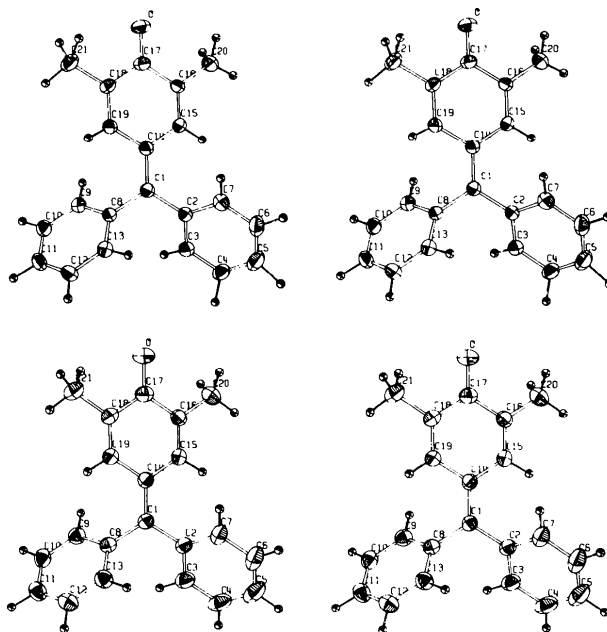
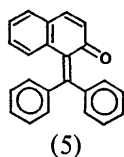


Fig. 1. Stereoscopic views of the molecules in the (1 α) (top) and (1 β) forms (bottom).

Table 5. Bond lengths (Å) and angles (°) in the forms (1 α) and (1 β)

	(1 α)	(1 β)		(1 α)	(1 β)
C(1)–C(2)	1.484 (3)	1.481 (4)	C(10)–C(11)	1.379 (4)	1.376 (5)
C(1)–C(8)	1.484 (3)	1.487 (3)	C(11)–C(12)	1.379 (4)	1.372 (5)
C(1)–C(14)	1.376 (3)	1.379 (3)	C(12)–C(13)	1.382 (4)	1.386 (4)
C(2)–C(3)	1.403 (4)	1.387 (4)	C(14)–C(15)	1.448 (3)	1.449 (4)
C(2)–C(7)	1.393 (4)	1.405 (4)	C(14)–C(19)	1.458 (3)	1.456 (4)
C(3)–C(4)	1.387 (4)	1.397 (4)	C(15)–C(16)	1.345 (3)	1.339 (4)
C(4)–C(5)	1.379 (6)	1.367 (5)	C(16)–C(17)	1.470 (3)	1.466 (4)
C(5)–C(6)	1.368 (6)	1.388 (5)	C(16)–C(20)	1.503 (4)	1.515 (4)
C(6)–C(7)	1.389 (4)	1.386 (5)	C(17)–C(18)	1.466 (3)	1.455 (4)
C(8)–C(9)	1.395 (3)	1.394 (4)	C(17)–O	1.244 (3)	1.242 (4)
C(8)–C(13)	1.395 (3)	1.391 (4)	C(18)–C(19)	1.348 (3)	1.353 (4)
C(9)–C(10)	1.386 (4)	1.400 (4)	C(18)–C(21)	1.506 (4)	1.510 (4)
C(2)–C(1)–C(8)	116.1 (2)	116.0 (2)	C(11)–C(12)–C(13)	120.1 (3)	120.2 (3)
C(2)–C(1)–C(14)	122.3 (2)	123.1 (2)	C(8)–C(13)–C(12)	120.8 (2)	120.6 (3)
C(8)–C(1)–C(14)	121.6 (2)	120.9 (2)	C(15)–C(14)–C(19)	116.1 (2)	116.1 (2)
C(3)–C(2)–C(7)	118.0 (2)	117.9 (3)	C(1)–C(14)–C(15)	122.9 (2)	122.8 (2)
C(1)–C(2)–C(3)	120.3 (2)	120.7 (2)	C(1)–C(14)–C(19)	121.0 (2)	121.0 (2)
C(1)–C(2)–C(7)	121.7 (2)	121.4 (2)	C(14)–C(15)–C(16)	123.2 (2)	122.9 (3)
C(2)–C(3)–C(4)	120.2 (3)	121.5 (3)	C(17)–C(16)–C(20)	118.2 (2)	117.6 (3)
C(3)–C(4)–C(5)	121.0 (3)	119.8 (3)	C(15)–C(16)–C(17)	119.7 (2)	120.2 (3)
C(4)–C(5)–C(6)	119.4 (4)	119.9 (3)	C(15)–C(16)–C(20)	122.1 (2)	122.1 (3)
C(5)–C(6)–C(7)	120.7 (3)	120.6 (3)	C(18)–C(17)–O	121.2 (2)	121.1 (3)
C(2)–C(7)–C(6)	120.8 (3)	120.3 (3)	C(16)–C(17)–C(18)	118.2 (2)	118.0 (2)
C(9)–C(8)–C(13)	118.3 (2)	118.6 (3)	C(16)–C(17)–O	120.7 (2)	120.8 (3)
C(1)–C(8)–C(9)	121.0 (2)	120.5 (2)	C(19)–C(18)–C(21)	122.3 (2)	121.2 (3)
C(1)–C(8)–C(13)	120.6 (2)	120.8 (2)	C(17)–C(18)–C(19)	119.8 (2)	120.1 (3)
C(8)–C(9)–C(10)	120.6 (2)	120.4 (3)	C(17)–C(18)–C(21)	117.9 (2)	118.8 (3)
C(9)–C(10)–C(11)	120.1 (2)	119.5 (3)	C(14)–C(19)–C(18)	122.8 (2)	122.5 (3)
C(10)–C(11)–C(12)	120.1 (3)	120.6 (3)			

than those found in the naphthoquinone derivative (5) (Duesler, Lewis, Curtin & Paul, 1978).



The angles found between the planes of the various rings also minimize the steric interactions. Rather than the ideal completely planar sp^2 -conjugated system [C(8), C(1), C(2), C(14), C(15), C(16), C(17), C(18), C(19)], the quinone ring is tilted 21.1° (1α) and 18.9° (1β) from the best plane through C(1), C(2), C(8), C(14); also, this latter plane makes angles of 39.9° (1α) and 38.7° (1β) with the phenyl ring C(2)–C(7) and angles of 47.4° and 47.3° with the phenyl ring C(8)–C(13). In this regard, the structures of the molecules of (1) in (1α) and (1β) are very similar to that reported for one of the forms of 2,6-dibromo-4-(α,α -diphenylmethylene)-1,4-benzoquinone (3) (Racine-Weisbuch, 1969). One of the consequences of these deviations from planarity is the molecular chirality. While individual molecules of (1) in both crystal forms are chiral if held in the conformation determined in the crystal, individual crystals of (1α) contain equal numbers of both enantiomers, whereas individual crystals of (1β) contain only one enantiomer. However, presumably there will be equal numbers of crystals of form (1β) of both chiralities.

Comparison of the crystal packing

The crystal structures of both (1α) and (1β) can be described conveniently in terms of layers of molecules.

Layers in the (001) planes or layers in the (011) planes could be selected for this description. In the present paper, we have chosen to describe the overall structure in terms of the layers in the (011) planes. The arrangement of such a layer of molecules in the (011) plane for (1β) is shown in Fig. 2. Some intermolecular contacts that define the arrangement of molecules in a layer for both forms are given in Table 7. From this table, it can be seen that the packing arrangement within the layer is quite similar in the two forms. The layer consists of pairs of adjacent rows of molecules running in the a direction with somewhat larger distances between adjacent pairs of rows. The small gaps so produced are filled in the assembly of the three-dimensional structure. In both forms, the molecules making up a layer are

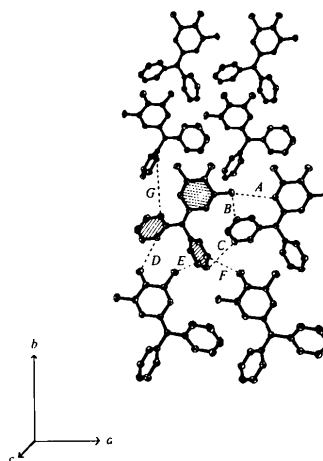


Fig. 2. The structure of a layer of molecules from the crystal of (1β). The reference molecule has the six-membered rings shaded. Distances that serve to define the layer are marked by letters and the values for the structures of (1α) and (1β) are given in Table 7.

Table 6. Details of planes of quinone rings in (1α) and (1β)

Distances (Å) are from the best plane through six ring atoms. The distances involving the atoms included in the best plane calculations are given in bold face. The best plane was calculated with weights $1/\sigma^2$, where σ is the standard deviation from the least-squares results.

	C(14)	C(15)	C(16)	C(17)	C(18)	C(19)	C(1)	C(2)	C(8)	C(20)	C(21)	O
(1α)	0.006 (2)	0.017 (2)	-0.021 (2)	0.002 (2)	0.022 (2)	-0.027 (2)	0.027 (2)	0.492 (2)	-0.413 (2)	-0.136 (4)	0.119 (4)	-0.009 (2)
(1β)	0.002 (2)	0.017 (3)	-0.024 (3)	0.011 (3)	0.012 (3)	-0.022 (3)	-0.040 (2)	0.324 (2)	-0.487 (3)	-0.142 (4)	0.049 (4)	0.016 (3)

Table 7. Important intermolecular contacts (Å) within a layer of molecules for both the (1α) and (1β) crystals

		(1α)*	(1β)†			(1α)*	(1β)†
C(21)···C(15) ¹	A‡	4.284 (4)	3.927 (4)	C(10)···C(20) ^{II}	E‡	3.650 (3)	3.594 (4)
C(21)···C(6) ¹	B	3.842 (4)	4.018 (4)	C(10)···O ^{III}	F	3.458 (3)	3.283 (3)
C(11)···C(4) ¹	C	3.614 (3)	3.819 (3)	C(6)···C(12) ^{IV}	G	6.794 (3)	5.901 (3)
C(3)···O ^{II}	D	4.228 (3)	4.764 (3)				

* For (1α), the equivalent positions are: (I) $1 + x, y, z$; (II) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (III) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (IV) $-x, \frac{1}{2} + y, -\frac{1}{2} - z$.

† For (1β), the equivalent positions are: (I) $1 + x, y, z$; (II) $1 - x, -\frac{1}{2} + y, 2\frac{1}{2} - z$; (III) $2 - x, -\frac{1}{2} + y, 2\frac{1}{2} - z$; (IV) $1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$.

‡ The capital letters refer to the contacts shown in Fig. 2.

generated either by a screw axis (along the **b** axis) or an axial translation (**a**— and **b** + **c**—). Thus a layer is made up of molecules of the same chirality. The assembly of layers to generate the entire crystal structure is different in the two forms. In Fig. 3 are shown stereoviews along the **a** axis of the assembly of layers in both forms. In both crystals every second layer (separated by the *c* axial length) is identical. However, in the crystal of (1 α), adjacent layers in the **c** direction are assembled by the operation of screw axis (along the **a** and **c** axes) thus preserving chirality, while in the racemic crystal of (1 α), adjacent layers in the **c** direction are assembled by the operation of glide planes (in the **c** direction) and centers of symmetry. Some intermolecular contacts between molecules in adjacent layers are given in Table 8.*

Evidence for a possible phase transition

The powder data (Table 4) provide evidence for a phase transition. The *d* spacings for the 100, 110, and 120 reflections of the (1 α) crystals are significantly different from any *d* spacings for the (1 β) crystals. Correspondingly, the *d* spacings for the 110 and 002 reflections of the (1 β) crystals are different from any

* See deposition footnote.

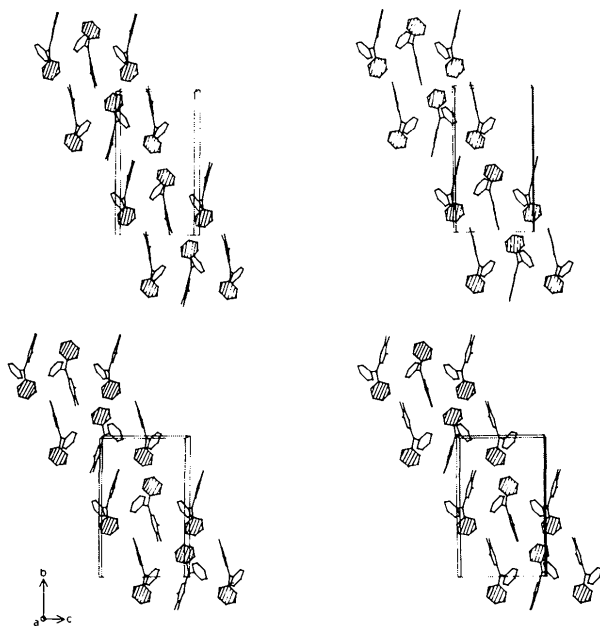


Fig. 3. Stereoscopic views of the manner in which three layers parallel to (011) are assembled in the structures of (1 α) (top) and (1 β) (bottom). Layers are viewed edge-on. The outline of the unit cell is shown. The C(2)—C(7) phenyl ring is shaded in all molecules to bring out the relationship between molecules in adjacent layers.

calculated for the (1 α) crystals. Powder picture *A* can only be matched by assuming a mixture of microcrystals of forms (1 α) (the major component) and (1 β); it is necessary to require the presence of some (1 β) to explain the $d = 5.47$ Å line which is caused by the very strong 002 reflection of the (1 β) form. However, powder picture *B* can be matched by assuming only the presence of microcrystals of form (1 β). The diffraction lines in picture *A* are broader and less sharply defined than those in picture *B*; this feature may also be an indication that picture *A* represents a mixture. These characteristics, which were observed for several different samples, are suggestive of a phase transition of form (1 α) converting to (1 β) at a temperature less than 383 K. It appears that grinding of crystals of (1 α) prior to heating was necessary to effect the transformation. It should be noted that the product of the solid-state dehydration of (2) is microcrystalline and gives a powder pattern corresponding to that of form (1 β) (Lewis, Curtin & Paul, 1979). No evidence was found for the intermediacy of (1 α) in this dehydration.

Relationship between the crystal forms (1 α) and (1 β)

Although the details of the transformation of (1 α) to (1 β) are not established at this time, it is interesting to speculate on the requirements for conversion of structure (1 α) to (1 β). The conversion may be visualized by considering the relationship of the respective molecules of (1) in the two forms in adjacent layer (011) planes (Fig. 3). In crystals of form (1 α), neighboring molecules (in the **c** direction) of adjacent layers are positioned such that the angle between the quinone-like rings [or the C(1)—C(14) vectors] is $\sim 120^\circ$. In form (1 β), the corresponding angle is 180° . These angular relationships are shown in a simplified schematic drawing (Fig. 4).

The gross structural relationship between molecules of adjacent layers in form (1 β) may be obtained from those in (1 α) by an approximate 60° rotation of every molecule in alternate layers. The 60° rotation around the C(1)—C(1) vector of neighboring molecules (in the **c** direction) in adjacent layers would result in the same net orientation of the quinone-like rings in (1 α) as in (1 β). However, in addition to such an overall molecular rotation, inversion of chirality of adjacent layers is necessary to generate the structure of (1 β) from (1 α). This can be accomplished by rotation of the phenyl rings in the molecules of (1 α) so that only one enantiomer is present. Since each layer plane of molecules in (1 α) is comprised of only one enantiomer and alternate layers are comprised of enantiomers of different configuration, only molecules of alternate layers must change 'handedness' to generate the structure of the (1 β) form. Some characteristics of the

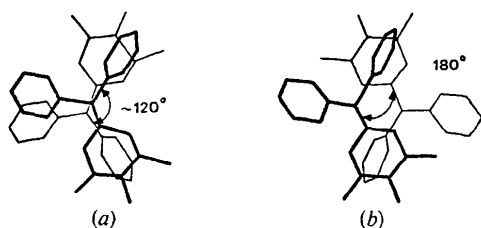


Fig. 4. Relative orientation of neighboring molecules in adjacent layers: (a) for (1 α), (b) for (1 β).

phase transition of (1 α) to (1 β) are reminiscent of the transition reported for binaphthyl (Pincock & Wilson, 1971; Pincock, Perkins, Ma & Wilson, 1971). While the transformation (1 α) to (1 β) involves a conversion from a racemic space group to a chiral one, we have not been able to measure the optical purity of single crystals as had been done with binaphthyl.

It is also of interest that a thermally induced transition of a monoclinic form ($\beta \approx 90^\circ$) to an orthorhombic form of 2,3-dimethyl-1,4-naphthoquinone has been reported (Breton, Chanh & Housty, 1976) but complete structures of the two forms were not reported. It should also be noted that, whereas (4-hydroxy-3,5-dimethylphenyl)diphenylmethanol (2) and its 3,5-dibromo analog (4) are isostructural (Stora, 1971; Lewis, Curtin & Paul, 1979), there is no such relationship between any of the three forms of (1) and the two

forms of its 2,6-dibromo analog (3) that have been studied by X-ray methods (Racine-Weisbuch, 1969).

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References

- BRETON, M., CHANH, N. B. & HOUSTY, J. (1976). *Mol. Cryst. Liq. Cryst.* **35**, 261–266.
 DIETERICH, D. A. (1973). PhD Thesis, Univ. of Illinois, Urbana, pp. 239–240.
 DUESLER, E. N., LEWIS, T. W., CURTIN, D. Y. & PAUL, I. C. (1978). *Acta Cryst.* **B34**, 985–988.
 DUESLER, E. N., LEWIS, T. W., CURTIN, D. Y. & PAUL, I. C. (1980). *Acta Cryst.* **B36**, 166–168.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–102. Birmingham: Kynoch Press.
 LEWIS, T. W., CURTIN, D. Y. & PAUL, I. C. (1979). *J. Am. Chem. Soc.* **101**, 5717–5725.
 PINCOCK, R. E., PERKINS, R. R., MA, A. S. & WILSON, K. R. (1971). *Science*, **174**, 1018–1020.
 PINCOCK, R. E. & WILSON, K. R. (1971). *J. Am. Chem. Soc.* **93**, 1291–1292.
 RABINOVICH, D. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. B*, pp. 127–131.
 RACINE-WEISBUCH, M. (1969). *C. R. Acad. Sci. Sér. C*, **269**, 99–102.
 STORA, C. (1971). *Bull. Soc. Chim. Fr.* pp. 2153–2160.

Acta Cryst. (1980). **B36**, 77–81

Structure and Absolute Configuration of (*R*)-Alaproclate [2-(4-Chlorophenyl)-1,1-dimethylethyl 2-Aminopropanoate] Hydrochloride, a Selective Inhibitor of Neuronal 5-Hydroxytryptamine Uptake

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Abstract

The crystal structure and absolute configuration of (*R*)-alaproclate (pINN), 2-(4-chlorophenyl)-1,1-dimethylethyl 2-aminopropanoate hydrochloride, a compound which selectively inhibits neuronal 5-hydroxytryptamine uptake, have been determined. (*R*)-alaproclate hydrochloride hydrate, C₁₃H₁₈ClNO₂·HCl·H₂O, crystallizes in space group *P2*₁ with

$a = 15.247(7)$, $b = 7.036(2)$, $c = 7.916(3)$ Å, $\beta = 97.81(4)^\circ$ and $Z = 2$. The structure was solved using the heavy-atom method. Full-matrix least-squares refinement resulted in a final *R* value of 0.05. The absolute configuration was determined by measuring Bijvoet differences. Potential-energy maps for a free molecule have been calculated. The calculations indicate that the side chain is flexible and may exist in several conformations with minor differences in potential energy.