Crystal data

$C_{21}H_{25}N$
M_r = 291.42
Monoclinic
$P2_1/n$
a = 14.939 (3) Å
b = 6.078 (4) Å
c = 19.740 (2) Å
β = 102.345 (12)°
V = 1750.9 (11) Å^3
Z = 4
D_x = 1.106 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 27–29°
μ = 0.475 mm^{-1}
T = 240 K
Plate
0.50 × 0.40 × 0.05 mm
Colourless

Data collection

Rigaku AFC-7R diffractometer
2θ–ω scans
Absorption correction: none
2706 measured reflections
2595 independent reflections
2224 reflections with $I > 2\sigma(I)$

R_{int} = 0.086
θ_{max} = 60°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = -22 \rightarrow 21$
3 standard reflections
every 150 reflections
intensity decay: −0.22%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.153
S = 1.041
2595 reflections
200 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1034P)^2 + 0.2489P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.062
$\Delta\rho_{max}$ = 0.192 e Å^{-3}
$\Delta\rho_{min}$ = −0.184 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0028 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.144 (2)	C1—C2	1.443 (2)
C4—C5—C6	117.67 (14)	C10—C11—C12	116.91 (14)
C9—C8—C13	117.32 (14)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1062). Services for accessing these data are described at the back of the journal.

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Complex of (−)-Morphine with β-Phenylhydracrylic Acid†

MARTIN LUTZ AND ANTHONY L. SPEK

Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands.
E-mail: m.lutz@chem.uu.nl

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Abstract

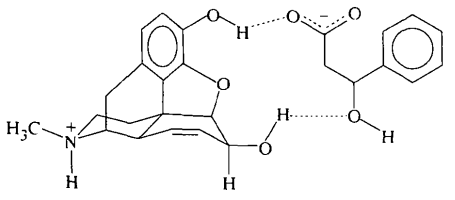
The crystal structure of the complex of (−)-morphine with (*S*)-β-phenylhydracrylic acid, $C_{17}H_{20}NO_3^+.C_9H_9O_3^-$, is reported. There are no major differences in the conformation of the piperidine ring of morphine compared with other protonated morphines. The staggered conformation of the central bond in the free form of β-phenylhydracrylic acid changes to another staggered conformation in the morphine complex. This conformational change is induced by intermolecular hydrogen bonds.

Comment

Morphine is the most important component of *papaver somniferum* extracts, which have been used as pain-alleviating medicine since ancient times. From a chemical point of view, morphine would be an interesting agent for resolving stereoisomers, but its

† Systematic names: (5α,6α)-7,8-didehydro-4,5-epoxy-17-methylmorphinan-3,6-diol (CAS-No. 57-27-2) and (*S*)-3-hydroxy-3-phenylpropanoic acid (CAS-No. 36567-72-3).

use for this purpose is nearly impossible because of the controlled distribution of this drug. In the present study, we investigate the interaction of morphine with a β-hydroxycarboxylic acid, namely, β-phenylhydracrylic acid. Because of the limited knowledge of the morphine receptor interaction, it is interesting to determine the conformational changes induced by hydrogen-bonding interactions with morphine.



(I)

The title compound, (I), with the numbering scheme, is shown in Fig. 1. The carboxy group of the β-phenylhydracrylic acid is deprotonated and the amino group of morphine is protonated. The morphine and acid molecules are linked by hydrogen bonds. Both hydroxy groups of morphine act as hydrogen-bond donors, with the carboxy and hydroxy groups of the same acid anion as the acceptors. The carboxy group is an acceptor for a hydrogen bond from a translated morphine molecule (at x, $y+1$, $z-1$), with the amino group as donor. The hydroxy group of the acid is the donor in a hydrogen bond to a third morphine molecule (at $x-1$, y, z), with the phenolic group as the acceptor. This pattern of hydrogen bonding builds up a two-dimensional network with [01$\bar{1}$] and [100] as the base vectors.

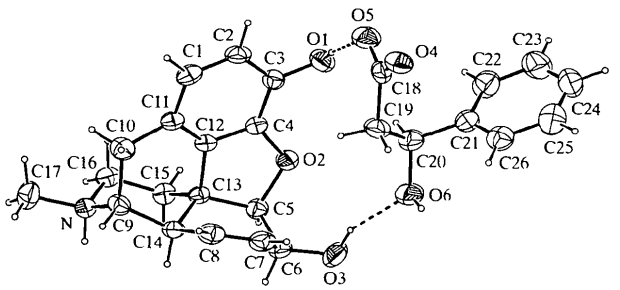


Fig. 1. Displacement ellipsoid (50% probability) plot (*PLATON*; Spek, 1998) of the title complex.

The physiological effectiveness of morphine seems mainly dependent on the conformation of the piperidine ring, the stereochemistry at the N atom or the accessibility of the protonated N atom by the receptor (Kolb, 1987). A ring-puckering analysis (Evans & Boeyens, 1989; Spek, 1998) of the piperidine ring of the title compound results in the parameters Q = 0.614 (3) Å, θ = 10.4 (3)° and φ = 89.5 (15)°, which correspond to a chair conformation with a slight deformation towards a twist-boat conformation. These puckering parameters are essentially the same as those found in morphine hydrochloride trihydrate (Gylbert, 1973) and di(morphine) dihydrogensulfate pentahydrate (Wongweichintana *et al.*, 1984). The stereochemistry at the N atom is also the same in all three cases, so that we can state that the stereochemistry of the protonated piperidine ring of morphine is independent of the counter-ions. A comparison with the crystal structure of morphine hydroiodide dihydrate (Mackay & Hodgkin, 1955) cannot be taken into account because of inaccurate geometrical details of that structure.

The β-phenylhydracrylic acid molecule shows a different conformation in the crystal structure of the morphine complex compared with its conformation in the free form (Cesario & Guilhem, 1974). Not only has the conformation of the carboxy group changed, as would be expected from the different hydrogen-bonding pattern, but the conformation about the central C_α—C_β bond has also changed dramatically, by about 120°. *MNDO* (Dewar & Thiel, 1977) calculations show that the rotational barrier for this bond is quite low (3.3 kcal mol^{-1}; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}), with the three staggered conformations at energy minima. The energy difference between these minima is only 1.1 kcal mol^{-1}. We can therefore assume that the barrier between the staggered conformation of the free compound and the staggered conformation of the morphine complex can be easily overcome by different hydrogen-bonding patterns.

Experimental

Crystals were obtained by slow evaporation of a 1:1 solution of (−)-morphine and (*S*)-β-phenylhydracrylic acid in water.

Crystal data

$C_{17}H_{20}NO_3^+.C_9H_9O_3^-$
M_r = 451.50
Triclinic
$P\bar{1}$
a = 6.6977 (7) Å
b = 7.9438 (5) Å
c = 10.8100 (13) Å
α = 72.643 (8)°
β = 85.549 (9)°
γ = 88.011 (7)°
V = 547.26 (9) Å^3
Z = 1
D_x = 1.370 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.72–14.09°
μ = 0.097 mm^{-1}
T = 293 (2) K
Block
0.30 × 0.25 × 0.25 mm
Brown

Data collection

Enraf–Nonius CAD-4T diffractometer

R_{int} = 0.091
θ_{max} = 27.49°

$\omega/2\theta$ scans
Absorption correction: none
4473 measured reflections
4325 independent reflections
3016 reflections with $I > 2\sigma(I)$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.122$
$S = 1.049$
4325 reflections
314 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.0076P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.282$ e Å^{-3}
$\Delta\rho_{min} = -0.211$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N—C17	1.485 (4)	O4—C18	1.240 (4)
N—C16	1.490 (4)	O5—C18	1.255 (4)
N—C9	1.515 (4)		
C17—N—C16	111.1 (2)	C17—N—H1	102 (2)
C17—N—C9	114.0 (2)	C16—N—H1	109 (2)
C16—N—C9	112.8 (2)	C9—N—H1	107 (2)
O4—C18—C19—C20	−118.2 (3)	O6—C20—C21—C22	117.5 (3)
O5—C18—C19—C20	62.1 (4)	C19—C20—C21—C22	−117.3 (3)
C18—C19—C20—O6	175.6 (3)	O6—C20—C21—C26	−63.1 (4)
C18—C19—C20—C21	49.1 (4)	C19—C20—C21—C26	62.1 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N—H1···O4^{i}	0.91 (4)	1.72 (4)	2.620 (3)	171 (3)
O1—H2···O5	0.82 (4)	1.74 (4)	2.535 (3)	166 (4)
O3—H3···O6	0.84 (4)	1.99 (4)	2.775 (4)	156 (4)
O6—H21···O1^{ii}	0.89 (4)	1.98 (5)	2.820 (4)	155 (4)

Symmetry codes: (i) $x, y-1, 1+z$; (ii) $x-1, y, z$.

The enantiomorph was chosen with respect to the known stereochemistry of (−)-morphine. R_{int} is based on only 148 reflections; if Friedel pairs are merged, $R_{int} = 0.0495$. All H atoms were located in a difference electron-density map. The positions of the ammonium and hydroxy H atoms were allowed to refine with individual isotropic displacement parameters. All other H atoms were constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C)$ for methyl H atoms].

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1054). Services for accessing these data are described at the back of the journal.

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N,N'-Bis(2-phenethyl)perylene-3,4:9,10-bis-(dicarboximide)

JIN MIZUGUCHI

Department of Applied Physics, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan. E-mail: mizuj@ed.ynu.ac.jp

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Abstract

The molecule of the title compound, $C_{40}H_{26}N_2O_4$, belongs to point group C_i. The perylene ring system is entirely planar, but is not fully delocalized, as shown by the fact that some C—C bonds are significantly longer compared with those of normal aromatic compounds. The phenyl rings at both ends of the molecule are not completely parallel to the plane of the perylene skeleton, but are slightly twisted in the same direction by about 2.7 (2)°.

Comment

N,N'-Bis(2-phenethyl)perylene-3,4:9,10-bis(dicarboximide), (I), is a commercial black pigment based on the