C2—C3—C4	112.4 (2)	C6—N—C7	123.0 (2)
C2—C3—C6	121.5 (2)	N—C7—C8	111.3 (2)
C4—C3—C6	126.1 (2)		

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(7,9-Diphenylcyclopenta[*a*]acenaphthadien-6b-yl)ethylbromide

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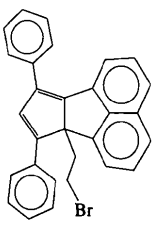
Abstract

The reaction between (7,9-diphenylcyclopenta[*a*]acenaphthadienyl)lithium and 1,2-dibromoethane resulted in the formation of the title compound, 6b-(2-bromoethyl)-7,9-diphenyl-6b*H*-cyclopenta[*a*]acenaphthylene, $C_{29}H_{21}Br$. Crystals suitable for X-ray structure determination were obtained from acetone.

Comment

The discovery of chiral group IV metallocene dichlorides as catalysts in stereospecific α-olefin polymerization has stimulated intensive research in academia as well as in industry for more than a decade now (Brintzinger, Fischer, Mülhaupt, Rieger & Waymouth, 1995). A well established way of synthesizing C_2-symmetric *ansa*-metallocenes is to prepare the ligand precursors by the reaction of cyclopentadienyl anions with 1,2-dibromoethane (Wild, Zsolnai, Huttner & Brintzinger, 1982; Alt, Milius & Palackal, 1994). Although we have used (7,9-diphenylcyclopenta[*a*]acenaphthadienyl)lithium, (2), for the preparation of unsymmetric *ansa*-zirconocenes bearing two different cyclopentadienyl fragments in the ethylene bridge (Rieger, Repo & Jany, 1994), it was not possible to prepare a C_2-symmetric ligand precursor by the reaction of (2) with 1,2-dibromoethane. Instead of the expected disubstitution, only monosubstitution of one Br atom occurred with 7,9-diphenylcyclopenta[*a*]acenaphthadienyl at the sterically and electronically unfavored 3-position of the five-membered ring, to give the title compound, (1) (Fig. 1).



(1)

If the structure of (1) in the solid state is compared with that of 2-(7,9-diphenylcyclopenta[*a*]acenaphthadien-6b-yl)-2-phenylethanol, (3) (Repo, Klinga, Leskelä, Polamo & Rieger, 1996), the same unequal C—C distances in the naphthalene unit [*e.g.* C12—C13 1.340 (13) and C13—C14 1.429 (11) Å] can be found. The bond lengths of the formally C—C single-bonded phenyl substituents [C4—C18 1.464 (10) and C6—C24 1.478 (10) Å] correspond to C_{sp^2}—C_{aryl} distances (Allen *et al.*, 1987; Norman, 1978). This is also indicated by the bright yellow luminescence of (1) in solution, which can be excited both by UV and visible light. Around the quaternary C3 atom, bond lengths [*e.g.* C2—C3 1.589 (9) and C3—C4 1.507 (9) Å], as well as bond angles [C4—C3—C15 125.0 (6), C7—C3—C15 101.2 (5) and C4—C3—C7 103.9 (6)°], are somewhat distorted from ideal tetrahedral values. There is no evidence of intermolecular interactions in the solid state other than van der Waals interactions.

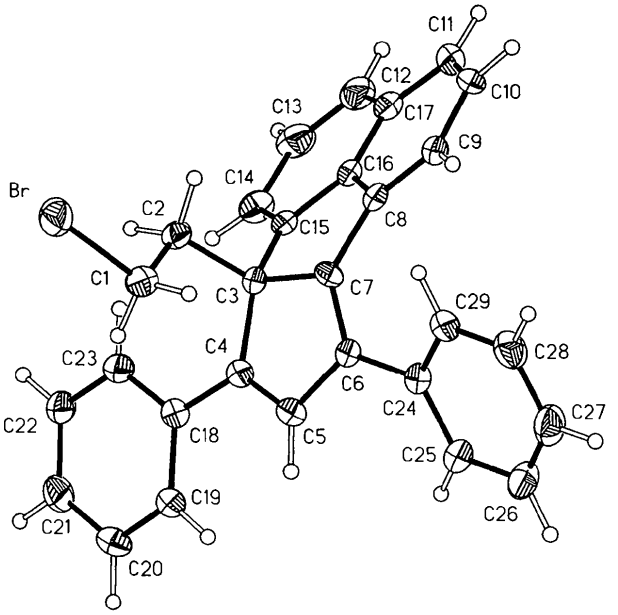


Fig. 1. View of the title compound, $C_{29}H_{21}Br$, with atom labels and displacement ellipsoids drawn at the 30% probability level.

Experimental

7,9-Diphenylcyclopenta[*a*]acenaphthadiene was prepared according to literature procedures (Ried, Merkel & Herrmann, 1971). This compound (10.00 g, 29.2 mmol) was dissolved in THF and treated dropwise with 18.2 ml *n*-buthyllithium (1.6 *M* in hexane) at 273 K to form compound (2). The reaction mixture was allowed to warm to ambient temperature and further reacted with 1.26 ml of 1,2-dibromoethane (2.74 g, 14.6 mmol). After stirring overnight, THF was evaporated and the solid residue was suspended in an aqueous solution of NH_4Cl, thoroughly extracted with CH_2Cl_2, dried over Na_2SO_4 and filtered. The organic layer was evaporated and the crude product chromatographed over silica (toluene/hexane 1:2) leading to yellow crystals of (1) (5.3 g, 11.8 mmol, 81%). ^1H NMR ($CDCl_3$): 2.59–3.37 (*m*, 4H, ethylbromide CH_2), 7.10–8.12 (*m*, 17H, aromatic H) p.p.m.

Crystal data

$C_{29}H_{21}Br$	Mo $K\alpha$ radiation
M_r = 449.37	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
Pbca	θ = 3–10°
a = 16.353 (9) Å	μ = 1.977 mm^{-1}
b = 30.264 (9) Å	T = 193 (2) K
c = 8.461 (8) Å	Prism
V = 4187 (5) Å^3	0.5 × 0.5 × 0.4 mm
Z = 8	Yellow
D_x = 1.426 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7*S* diffractometer	1936 reflections with $I > 2\sigma(I)$
ω scans	θ_{max} = 25.02°
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 19$
	$k = 0 \rightarrow 35$
	$l = 0 \rightarrow 10$
T_{min} = 0.350, T_{max} = 0.453	3 standard reflections every 200 reflections
2913 measured reflections	intensity decay: <2%
2913 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.005
$R(F)$ = 0.0712	$\Delta\rho_{max}$ = 1.060 e Å^{-3}
$wR(F^2)$ = 0.2757	$\Delta\rho_{min}$ = −1.148 e Å^{-3}
S = 1.119	Extinction correction: none
2869 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
271 parameters	
H atoms riding	
$w = 1/[\sigma^2(F_o^2) + (0.112P)^2 + 10.8P]$ where $P = (F_o^2 + 2F_c^2)/3$	

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

Br—C1	1.930 (8)	C3—C15	1.538 (10)
C1—C2	1.518 (11)	C4—C18	1.464 (10)
C2—C3	1.589 (9)	C6—C24	1.478 (10)
C3—C4	1.507 (9)	C12—C13	1.340 (13)
C3—C7	1.529 (9)	C13—C14	1.429 (11)
C4—C3—C2	111.4 (6)	C15—C3—C2	106.4 (5)
C7—C3—C2	107.4 (6)		

The intensity data were corrected for Lorentz and polarization effects and for absorption. All non-H atoms were anisotropically refined. H atoms were assigned displacement parameters 1.3 times those of the host atom (riding model). The four largest maxima/minima in the final difference map, of magnitude 0.90–1.15 e A^{-3}, were at 1.0–1.2 Å from the Br atom; others were less than 0.57 e A^{-3}.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1993). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*92.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anthranilic Acid–Picric Acid (2/1) Complex

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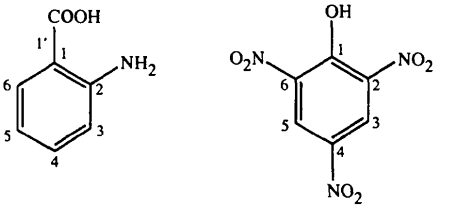
Abstract

The X-ray crystal structure of the 2:1 anthranilic acid–picric acid complex, $2C_7H_7NO_2.C_6H_3N_3O_7$, shows extensive stacking interactions, where picric acid is sandwiched between two crystallographically independent anthranilic acid molecules, with spacings of 3.29 and 3.33 Å. The carboxyl and amino groups of anthranilic acid are neutral and the former group is hydrogen bonded to the polar nitro and phenol O atoms of neighbouring picric acid molecules. The present results indicate the superior π-donating ability of anthranilic acid, as well as a superior hydrogen-bonding ability, in its interaction with an acceptor molecule such as picric acid.

Comment

It is known that picric acid functions not only as an acceptor to form π-stacking complexes with aromatic biomolecules, but also as an acidic ligand to form salts with polar biomolecules through specific electrostatic or hydrogen-bonding interactions. As part of a study estimating the π-stacking and hydrogen-bonding abilities of biomolecules (Nagata, In, Doi, Ishida & Wakahara, 1995; Nagata, In, Tomoo, Doi, Ishida & Wakahara, 1995), this paper deals with the X-ray crystal structure of a 2:1 anthranilic acid–picric acid complex. Because of the polar and aromatic characters of anthranilic acid, it is of interest to know whether the π-stacking or hydrogen-bonding ability function predominates in complex formation with picric acid.



2:1

Picric acid is found to be sandwiched by two crystallographically independent anthranilic acid molecules (Fig. 1), where the respective dihedral angles and mean interplanar spacings are 2.8 (5)° and 3.29 Å for the upper pair, and 1.4 (5)° and 3.33 Å for the lower one. No notable stacking interaction was observed between neighbouring anthranilic acid molecules. The carboxyl groups of the anthranilic acid molecules are hydrogen bonded to the polar atoms of neighbouring anthranilic acid and picric acid molecules (Fig. 2); two independent anthranilic acid molecules are linked to one another through O—H···O hydrogen bonds around the diad screw axis along the *b* axis (Table 2). Although the complex molecules are linked by O—H···O hydrogen bonds and O···O electrostatic interactions, it is significant that the amino group of anthranilic acid does not participate in any specific interaction.

The difference Fourier map indicated that the carboxyl and amino groups of anthranilic acid and the phenol group of picric acid are neutral. This is also suggested by the bond lengths and angles, and the intermolecular interaction pattern of the complex.

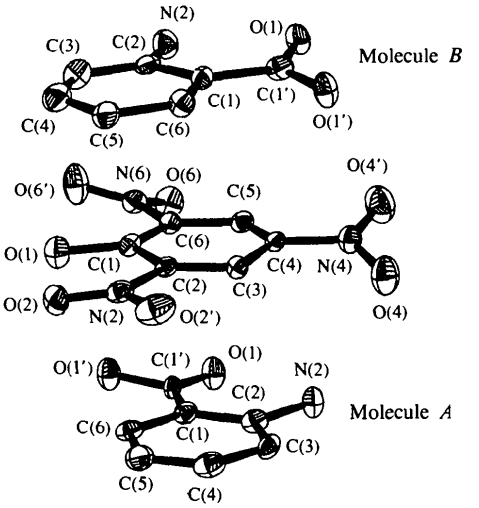


Fig. 1. The stacking interaction between the anthranilic and picric acid molecules. The upper and lower anthranilic acid molecules correspond to molecules *A* and *B*, respectively. H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.