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Structure of 5,5-Diphenylhydantoin–1-(4-Bromophenyl)-4-dimethylamino-2,3-dimethyl-3-pyrazolin-5-one (1:1)

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Abstract. $C_{15}H_{12}N_2O_2.C_{13}H_{16}BrN_3O$, M_r = 562·5, triclinic, $P\bar{1}$, a = 12·997 (8), b = 9·902 (5), c = 12·796 (9) Å, α = 113·21 (9), β = 118·18 (7), γ = 83·37 (19)°, U = 1329·0 Å^3, D_x = 1·405, D_m (n-heptane/CCl_4) = 1·408 Mg m^{-3}, Z = 2, μ = 1·74 mm^{-1}, $F(000)$ = 580, Mo $K\alpha$ radiation, λ = 0·71069 Å. The final R index was 0·033 for 2485 reflections. In the crystal, molecules of the title compound are held together by hydrogen bonds (NH···O) and weak charge-transfer interactions (O—Br), in the a-axis direction.

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Introduction. 5,5-Diphenylhydantoin (DPH) is used as an antiepileptic drug. This analysis was undertaken to obtain information concerning the interactions between DPH and 1-(4-bromophenyl)-4-dimethylamino-2,3-dimethyl-3-pyrazolin-5-one (BDDP). Single crystals (colorless plates) of the title compound were obtained by slow evaporation of an equimolar mixture of DPH and BDDP dissolved in acetone. Lattice parameters

Table 1. *Positional parameters and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{iso}(Å^2)
DPH				
C(1)	0·4999 (4)	0·7976 (4)	0·7086 (4)	3·50
O(1)	0·5843 (2)	0·8431 (3)	0·8132 (3)	4·97
N(1)	0·4893 (3)	0·6721 (3)	0·6063 (3)	3·30
C(2)	0·3848 (3)	0·6572 (4)	0·4954 (4)	3·10
O(2)	0·3577 (2)	0·5567 (3)	0·3903 (2)	3·40
N(2)	0·3244 (2)	0·7709 (3)	0·5265 (2)	3·14
C(3)	0·3830 (3)	0·8684 (4)	0·6629 (3)	2·95
C(4)	0·3149 (3)	0·8610 (4)	0·7315 (3)	3·31
C(5)	0·1945 (4)	0·8625 (4)	0·6728 (3)	3·59
C(6)	0·1319 (3)	0·8695 (4)	0·7378 (4)	4·19
C(7)	0·1888 (4)	0·8709 (4)	0·8600 (4)	4·36
C(8)	0·3059 (4)	0·8670 (5)	0·9168 (4)	5·07
C(9)	0·3709 (3)	0·8624 (5)	0·8546 (4)	4·53
C(10)	0·4064 (3)	1·0272 (4)	0·6826 (3)	3·40
C(11)	0·4148 (3)	1·0563 (4)	0·5898 (4)	4·21
C(12)	0·4403 (4)	1·1991 (5)	0·6099 (5)	5·49
C(13)	0·4577 (4)	1·3137 (5)	0·7227 (5)	5·62
C(14)	0·4503 (4)	1·2868 (4)	0·8149 (4)	5·48
C(15)	0·4241 (3)	1·1441 (4)	0·7966 (3)	4·45
H(1)	0·543 (3)	0·607 (3)	0·609 (3)	3·30
H(2)	0·257 (3)	0·791 (3)	0·468 (3)	3·14
H(5)	0·153 (3)	0·850 (3)	0·579 (3)	3·59
H(6)	0·041 (3)	0·864 (4)	0·689 (3)	4·19
H(7)	0·142 (3)	0·876 (4)	0·904 (3)	4·36
H(8)	0·347 (3)	0·868 (4)	0·998 (3)	5·07
H(9)	0·459 (3)	0·860 (4)	0·896 (3)	4·53
H(11)	0·394 (3)	0·979 (4)	0·506 (3)	4·21
H(12)	0·435 (3)	1·216 (4)	0·540 (3)	5·49
H(13)	0·480 (3)	1·417 (4)	0·743 (3)	5·62
H(14)	0·458 (3)	1·369 (4)	0·898 (3)	5·48
H(15)	0·414 (3)	1·126 (4)	0·858 (3)	4·45

	x	y	z	B_{iso}(Å^2)
BDDP				
Br	−0·19832 (5)	0·59219 (5)	0·54575 (4)	5·14
C(16)	−0·1597 (3)	0·6339 (4)	0·4357 (3)	3·58
C(17)	−0·1565 (4)	0·5199 (4)	0·3329 (4)	4·62
C(18)	−0·1251 (4)	0·5486 (4)	0·2537 (4)	4·31
C(19)	−0·0987 (3)	0·6932 (4)	0·2798 (3)	3·29
C(20)	−0·1051 (3)	0·8071 (4)	0·3809 (3)	3·24
C(21)	−0·1360 (3)	0·7786 (4)	0·4600 (3)	3·71
N(3)	−0·0645 (3)	0·7282 (3)	0·2019 (3)	3·16
N(4)	−0·1236 (3)	0·6558 (3)	0·0672 (3)	3·39
C(22)	−0·2507 (4)	0·6666 (5)	0·0078 (4)	4·98
C(23)	−0·0570 (3)	0·6985 (4)	0·0247 (3)	3·01
C(24)	−0·0996 (4)	0·6518 (4)	−0·1168 (3)	4·43
C(25)	0·0421 (3)	0·7781 (4)	0·1250 (3)	3·08
N(5)	0·1327 (3)	0·8315 (3)	0·1154 (3)	3·81
C(26)	0·2385 (4)	0·7579 (5)	0·1567 (5)	6·55
C(27)	0·1545 (4)	0·9898 (5)	0·1767 (5)	6·04
C(28)	0·0411 (3)	0·7960 (4)	0·2422 (4)	3·10
O(3)	0·1160 (2)	0·8547 (2)	0·3570 (2)	3·40
H(17)	−0·173 (3)	0·417 (4)	0·313 (3)	4·62
H(18)	−0·130 (3)	0·462 (4)	0·168 (3)	4·31
H(20)	−0·090 (3)	0·913 (3)	0·396 (3)	3·24
H(21)	−0·144 (3)	0·859 (4)	0·535 (3)	3·71
H(221)	−0·267 (3)	0·770 (4)	0·019 (3)	4·98
H(222)	−0·281 (3)	0·606 (4)	−0·084 (4)	4·98
H(223)	−0·284 (3)	0·627 (4)	0·038 (3)	4·98
H(241)	−0·039 (3)	0·681 (4)	−0·127 (3)	4·43
H(242)	−0·117 (3)	0·549 (4)	−0·161 (3)	4·43
H(243)	−0·168 (3)	0·708 (4)	−0·147 (3)	4·43
H(261)	0·220 (4)	0·657 (5)	0·108 (4)	6·55
H(262)	0·296 (4)	0·789 (4)	0·143 (4)	6·55
H(263)	0·277 (4)	0·781 (4)	0·246 (4)	6·55
H(271)	0·210 (4)	1·020 (4)	0·158 (4)	6·04
H(272)	0·082 (4)	1·034 (4)	0·150 (4)	6·04
H(273)	0·185 (4)	1·030 (4)	0·267 (4)	6·04

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were obtained by a least-squares method from the setting angles of 18 reflections. Three-dimensional intensity data with $(\sin\theta)/\lambda \leq 0.6497$ Å^{-1} were collected on a Rigaku four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation from a crystal with dimensions 0·4 × 0·4 × 0·5 mm. A total of 2485 independent reflections were considered as observed [$I > 3.0\sigma(I)$] and used in this analysis. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by the standard heavy-atom method. Because there were too many variable parameters (418), including anisotropic temperature factors for the nonhydrogen atoms, the structure was refined by full-matrix least-squares calculations with parameters grouped into three blocks to yield $R = 0.033$. Isotropic temperature factors of 28 H atoms were fixed to be equal to the isotropic temperature factors of their parent atoms (3·14–6·55 Å^2). Anomalous dispersion for Br was taken into account in the structure factor calculation. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Positional parameters are shown in Table 1.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35429 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

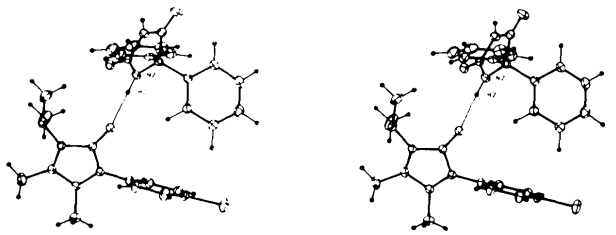

Fig. 1. Stereoscopic drawing of the title compound.

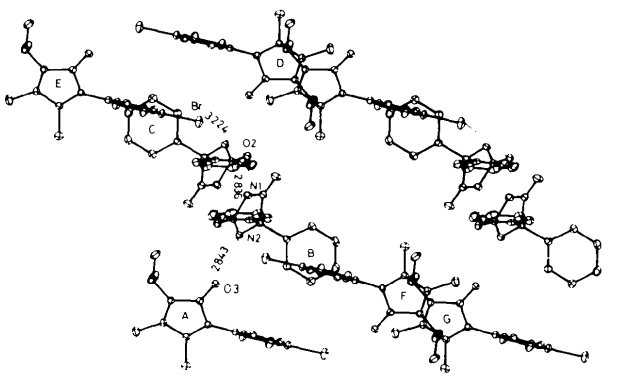

Fig. 2. Packing diagram of the title compound. Hydrogen bonding (– – –); charge transfer (——). The axial directions are $a \searrow$, $c \rightarrow$ and b^* out of the page.

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

Estimated standard deviations are given in parentheses.

5,5-Diphenylhydantoin

C(1) O(1)	1·204 (5)	C(5) -C(6)	1·393 (8)
C(1) N(1)	1·365 (5)	C(6)–C(7)	1·373 (7)
C(1) -C(3)	1·543 (6)	C(7)- C(8)	1·345 (7)
N(1) C(2)	1·393 (5)	C(8) -C(9)	1·395 (9)
C(2) -O(2)	1·225 (5)	C(10) -C(11)	1·380 (8)
C(2) -N(2)	1·334 (5)	C(10) -C(15)	1·391 (5)
N(2) -C(3)	1·464 (4)	C(11) C(12)	1·384 (7)
C(3)- C(4)	1·536 (7)	C(12)–C(13)	1·372 (7)
C(3) -C(10)	1·534 (6)	C(13)–C(14)	1·354 (10)
C(4)–C(5)	1·381 (6)	C(14) C(15)	1·394 (6)
C(4) -C(9)	1·383 (6)		

O(1) C(1)–N(1)	126·4 (4)	C(3) -C(4)--C(9)	122·0 (3)
O(1)- C(1) -C(3)	127·3 (4)	C(5) C(4) -C(9)	118·3 (4)
N(1) -C(1)- C(3)	106·3 (3)	C(4)–C(5)--C(6)	120·5 (4)
C(1) N(1) -C(2)	112·3 (4)	C(5) -C(6)- C(7)	120·4 (4)
N(1)–C(2) O(2)	124·3 (4)	C(6)- C(7) C(8)	119·3 (6)
N(1)- C(2) N(2)	107·3 (3)	C(7) -C(8)–C(9)	121·5 (5)
O(2) -C(2)- N(2)	128·3 (3)	C(4) -C(9)--C(8)	120·0 (3)
C(2)–N(2) C(3)	113·3 (3)	C(3)- C(10) -C(11)	120·7 (3)
C(1) -C(3)--N(2)	100·3 (3)	C(3)–C(10)–C(15)	120·5 (4)
C(1) --C(3)- C(4)	111·0 (4)	C(11)–C(10)–C(15)	118·7 (4)
C(1) -C(3) C(10)	109·7 (4)	C(10)–C(11)- C(12)	120·6 (4)
N(2) C(3) -C(4)	111·2 (3)	C(11) C(12)–C(13)	120·3 (6)
N(2) C(3) -C(10)	112·0 (4)	C(12) C(13)–C(14)	119·8 (5)
C(4) -C(3) C(10)	112·0 (3)	C(13) -C(14)–C(15)	121·0 (4)
C(3) -C(4)- C(5)	119·5 (4)	C(10) -C(15)–C(14)	119·7 (5)

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Br -C(16)	1·892 (5)	N(4)–C(22)	1·468 (6)
C(16) -C(17)	1·370 (6)	N(4)- C(23)	1·391 (7)
C(16)–C(21)	1·380 (6)	C(23) C(24)	1·500 (5)
C(17) C(18)	1·385 (9)	C(23)–C(25)	1·343 (5)
C(18) C(19)	1·381 (6)	C(25) -N(5)	1·419 (7)
C(19) C(20)	1·372 (5)	C(25)–C(28)	1·445 (7)
C(19) -N(3)	1·427 (7)	N(5)- C(26)	1·445 (6)
C(20)- C(21)	1·379 (7)	N(5)–C(27)	1·441 (5)
N(3) -N(4)	1·406 (5)	C(28)- O(3)	1·245 (4)
N(3)- C(28)	1·368 (6)		

Br -C(16)- C(17)	119·4 (4)	N(3)–N(4)–C(23)	104·8 (3)
Br- C(16) -C(21)	119·4 (3)	C(22) N(4) C(23)	119·5 (4)
C(17)–C(16)- C(21)	121·2 (5)	N(4)- C(23) -C(24)	119·8 (3)
C(16)- C(17)-C(18)	119·9 (4)	N(4) -C(23)–C(25)	110·5 (4)
C(17) C(18)–C(19)	118·8 (4)	C(24)–C(23)–C(25)	129·7 (5)
C(18) -C(19)- C(20)	120·9 (5)	C(23)–C(25)–N(5)	125·0 (4)
C(18)--C(19) N(3)	120·9 (4)	C(23)–C(25)- C(28)	108·4 (4)
C(20) C(19)–N(3)	118·2 (4)	N(5)- C(25) -C(28)	126·5 (3)
C(19)–C(20) C(21)	120·3 (4)	C(25)–N(5)–C(26)	112·8 (4)
C(16)–C(21) C(20)	118·7 (3)	C(25) -N(5)–C(27)	112·7 (4)
C(19)–N(3)- N(4)	120·4 (3)	C(26)--N(5)–C(27)	112·4 (4)
C(19) -N(3)–C(28)	126·0 (3)	N(3) C(28)–C(25)	104·6 (3)
N(4)- N(3)- C(28)	111·1 (4)	N(3)–C(28) O(3)	124·1 (5)
N(3) N(4) C(22)	114·8 (4)	C(25) C(28) O(3)	131·2 (4)

Discussion. Table 2 lists bond distances and angles. Table 3 contains the best planes and deviations of the atoms from them. Bond lengths and angles in DPH are reasonable in comparison with our previous results for diamminediaquabis(5,5-diphenylhydantoinato)-nickel(II) (Shimizu & Uno, 1980*a*) and diamminebis(5,5-diphenylhydantoinato)copper(II) (Shimizu & Uno, 1980*b*), and with those for DPH (Camerman & Camerman, 1971). O(1) atoms deviate from plane (1) by 0·123 (3) Å. Dihedral angles between planes (1) and (2), between planes (1) and (3) and

Table 3. *Least-squares planes and deviations* (Å) *of atoms from them*

The planes are expressed by $lx + my + nz = d$ in Å.

5,5-Diphenylhydantoin

Plane (1): $-0{\cdot}6010x - 0{\cdot}7631y + 0{\cdot}2376z = 3{\cdot}9311$
C(1) −0·034 (5), N(1) 0·024 (4), C(2) 0·000 (4), N(2) −0·022 (3), C(3) 0·032 (4), O(1)* −0·123 (3), O(2)* −0·011 (3), H(1)* 0·064 (36), H(2)* −0·137 (36)

Plane (2): $0{\cdot}0752x - 0{\cdot}9236y - 0{\cdot}3758z = 1{\cdot}3938$
C(4) −0·006 (4), C(5) 0·010 (4), C(6) −0·006 (4), C(7) −0·001 (4), C(8) 0·005 (5), C(9) −0·001 (5), C(3)* −0·126 (4)

Plane (3): $-0{\cdot}8908x + 0{\cdot}2080y - 0{\cdot}4041z = -4{\cdot}7317$
C(10) −0·000 (4), C(11) −0·001 (4), C(12) 0·000 (5), C(13) 0·002 (5), C(14) −0·003 (5), C(15) 0·002 (4), C(3)* −0·058 (4)

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Plane (4): $0{\cdot}5217x - 0{\cdot}8530y + 0{\cdot}0115z = 2{\cdot}2982$
N(3) −0·041 (4), N(4) 0·039 (4), C(23) −0·024 (4), C(25) 0·000 (4), C(28) 0·025 (4), C(19)* 0·190 (4), C(22)* −0·838 (5), C(24)* −0·082 (5), N(5)* 0·028 (4), O(3)* 0·117 (3)

Plane (5): $-0{\cdot}7772x + 0{\cdot}2242y - 0{\cdot}5880z = -0{\cdot}5460$
C(16) −0·013 (4), C(17) 0·008 (5), C(18) 0·003 (5), C(19) −0·010 (4), C(20) 0·005 (4), C(21) 0·006 (4), Br* −0·058 (1), N(3)* −0·032 (4)

* Atoms not included in the plane calculations.

between planes (2) and (3), are 55·2, 73·7 and 96·2° respectively. In BDDP bond distances and angles are similar to those found in BDDP itself (Shimizu & Uno, 1980*c*). The notable contact in Fig. 1 is the hydrogen bond between N(2)–H of hydantoin and O=C(28) of 3-pyrazoline. The pyrazoline–phenyl angle in the BDDP part is 52·9° and our result for BDDP itself is 36·6°. This difference in rotation about C–N is mainly brought about by the adjacent plane (2) of DPH. The dihedral angle between planes (2) and (5) is 92·6°; H(6)···H(21), 2·268 Å, is shorter than the sum of the van der Waals radii (Pauling, 1960). Fig. 2 is the packing diagram. Table 4 gives the hydrogen-bond and charge-transfer parameters. DPH molecules form dimers (*B*–*C*) *via* hydrogen bonds N(1)–H···O(2). In the *a*-axis direction, *A*–*B*–*C*–*D* chains as a unit are linked by weak O(2)–Br (*C*–*E* and *B*–*F*) charge-transfer interactions (Gaultier, Hauw & Schvoerer, 1971). O(1) atoms do not participate in any hydrogen bonds. No short contacts exist between *F* and *G*.

Table 4. *Intermolecular hydrogen bonds and the charge-transfer interaction*

Donors		Acceptors		Parameters	
N(2)–H(2)	*B* (i)	O(3)	*A* (i)	N(2)–H(2)	0·91 (3) Å
				N(2)···O(3)	2·843 (5)
				H(2)···O(3)	1·938 (31)
				N(2)–H(2)···O(3)	173·9 (24)°
N(1)–H(1)	*C* (ii)	O(2)	*B* (i)	N(1)–H(1)	0·89 (3) Å
				N(1)···O(2)	2·836 (7)
				H(1)···O(2)	1·952 (32)
				N(1)–H(1)···O(2)	171·2 (37)°
O(2)	*C* (ii)	Br	*E* (iii)	Br–C(16)	1·892 (5) Å
				O(2)···Br	3·224 (5)
				O(2)···Br C(16)	154·6 (1)°

Symmetry code: (i) x, y, z; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 + x, y, z$.
B and *C*: 5,5-diphenylhydantoin.
A and *E*: 1-(4-bromophenyl)-4-dimethylamino-2,3-dimethyl-3-pyrazolin-5-one.

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