Acta Cryst. (1990). C**46**, 1475–1477

Structures of 2,4-Dihydro-8-methoxy-2-(*p*-methoxyphenyl)-4,4-dimethyl-1*H*-[1]benzopyrano[4,3,2-*cd*]indol-1-one (I) and 2,4-Dihydro-8-methoxy-4,4-dimethyl-2-phenyl-1*H*-[1]benzopyrano[4,3,2-*cd*]indol-1-one (II)

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(*Received* 25 *August* 1989; *accepted* 17 *November* 1989)

Abstract. (I) $C_{24}H_{21}NO_4$, $M_r = 387{\cdot}44$, monoclinic, $P2_1/c$, $a = 8{\cdot}197\ (6)$, $b = 10{\cdot}907\ (6)$, $c = 21{\cdot}982\ (5)$ Å, $\beta = 93{\cdot}763\ (3)°$, $V = 1961{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$, $D_m = 1{\cdot}30$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}64$ mm^{-1}, $T = 293$ K, $F(000) = 816$, unit weights, $R = 0{\cdot}059$ for 2636 unique reflections with $I > 3\sigma(I)$. (II) $C_{23}H_{19}NO_3$, $M_r = 357{\cdot}41$, monoclinic, $P2_1/n$, $a = 5{\cdot}567\ (4)$, $b = 20{\cdot}763\ (6)$, $c = 15{\cdot}396\ (3)$ Å, $\beta = 92{\cdot}820\ (3)°$, $V = 1777{\cdot}43$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$, $D_m = 1{\cdot}34$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0{\cdot}63$ mm^{-1}, $T = 293$ K, $F(000) = 752$, $R = 0{\cdot}040$, $wR = 0{\cdot}041$ for 1356 unique reflections with $I > 3\sigma(I)$. The conformation of the pyran rings is a distorted boat in both compounds. The D_{2h} symmetry of the 1,4-cyclohexadiene is distorted towards half-chair and boat conformations in compounds (I) and (II), respectively.

Introduction. The title compounds [(I) and (II)] are condensation products of 2-[(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-oxy]-6-methoxy-3(2*H*)-benzofuranone with a 4-substituted aromatic amine (Chandrasekhar, 1989) in glacial acetic acid medium. The crystal structure analysis of these compounds was undertaken to confirm the structure assigned by IR and ^{1}H NMR data and to determine the size of the lactam ring.

Experimental. Compound (I): Brown prismatic single crystals were grown by slow evaporation of the compound in carbon tetrachloride, density measured by flotation. Intensity data were collected from a crystal of approximate dimensions 0·35 × 0·40 × 0·45 mm up to $(\sin\theta/\lambda) = 0{\cdot}62$ Å^{-1} with ω–2θ scan using crystal-monochromated Cu $K\alpha$ radiation. Cell parameters were refined by least-squares calculations from 25 reflections with $20 < \theta < 40°$ on an Enraf–Nonius CAD-4 automated diffractometer. Two strong reflections (1$\bar{2}$7 and 211) monitored periodically during data collection showed that the crystal was stable. Index range of unique data $-9 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 26$. 3800 reflections were collected of which 2636 unique reflections with $I > 3\sigma(I)$ were considered observed. Compound (II): Pale pink needle-shaped crystals were grown by slow evaporation from methanol. Density by flotation. Crystal dimensions 0·2 × 0·2 × 0·5 mm, data collected up to $(\sin\theta/\lambda) = 0{\cdot}63$ Å^{-1} with ω–2θ scan using crystal-monochromated Cu $K\alpha$ radiation. Unit-cell parameters from 22 reflections with $30 < \theta < 45°$ on an Enraf–Nonius CAD-4 automated diffractometer. Two strong reflections ($\bar{2}$83 and 15$\bar{2}$) monitored periodically during data collection showed that the crystal was stable. Index range of unique data $-6 \le h \le 6$, $0 \le k \le 25$, $0 \le l \le 18$. 1893 reflections collected of which 1356 unique reflections with $I > 3\sigma(I)$. Lp correction applied. For both (I) and (II) absorption and extinction were neglected.

The structures were solved by multisolution techniques using *SHELXS*86 (Sheldrick, 1986) and refined on F by least-squares methods with *SHELX*76 (Sheldrick, 1976). H-atom positions from difference Fourier maps at intermediate stages of refinement. Final refinement with non-H atoms anisotropically and H atoms isotropically converging to the following results. Compound (I): $R = 0{\cdot}059$ with unit weights. Quantity minimized was $\sum(|F_o| - K|F_c|)^2$, $(\text{shift/e.s.d.})_{\max} = 0{\cdot}046$. Maximum and minimum heights in final difference Fourier synthesis 0·19 and $-0{\cdot}21$ e Å^{-3}. Compound (II): $R = 0{\cdot}040$ and $wR = 0{\cdot}041$. Quantity minimized was $\sum w(|F_o| - K|F_c|)^2$ with $w = k'\{[|\sigma(F_o)|]^2 + g(|F_o|)^2\}^{-1}$ with $k' = 1{\cdot}3122$ and $g = 0{\cdot}001547$, $(\text{shift/e.s.d.})_{\max} = 0{\cdot}045$. Maximum and minimum heights in final difference Fourier synthesis are 0·13 and $-0{\cdot}24$ e Å^{-3}. For both (I) and (II) atomic scattering factors were taken from *SHELX*76 and the calculations were performed on a Siemens 7·580-E computer.

0108-2701/90/081475-03$03.00

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	U_{eq}
(*a*) Compound (I)				
N	0·7808 (4)	1·2657 (3)	0·1280 (2)	0·0634 (12)
C(1)	0·8105 (5)	1·1859 (4)	0·0791 (2)	0·0661 (15)
C(3)	0·5847 (5)	1·2568 (3)	0·2109 (2)	0·0609 (14)
C(4)	0·4494 (5)	1·1824 (4)	0·2373 (2)	0·0614 (14)
C(5)	0·3997 (5)	1·0692 (4)	0·2003 (2)	0·0605 (14)
O	0·4446 (3)	0·9276 (2)	0·1202 (1)	0·0642 (10)
C(7)	0·4994 (5)	0·7862 (4)	0·0450 (2)	0·0655 (15)
C(8)	0·5889 (5)	0·7453 (4)	−0·0031 (2)	0·0672 (16)
C(9)	0·7155 (5)	0·8151 (4)	−0·0237 (2)	0·0687 (16)
C(10)	0·7520 (5)	0·9255 (4)	0·0041 (2)	0·0641 (15)
C(11)	0·6579 (5)	1·2184 (3)	0·1631 (2)	0·0579 (14)
C(12)	0·4812 (5)	1·0337 (3)	0·1537 (2)	0·0561 (13)
C(13)	0·5393 (5)	0·8965 (3)	0·0722 (2)	0·0573 (13)
C(14)	0·6672 (5)	0·9684 (4)	0·0524 (2)	0·0581 (14)
C(15)	0·6986 (4)	1·0815 (3)	0·0860 (2)	0·0562 (13)
C(16)	0·6121 (4)	1·1046 (3)	0·1338 (2)	0·0534 (12)
C(17)	0·2993 (6)	1·2660 (4)	0·2405 (2)	0·0854 (19)
C(18)	0·5046 (6)	1·1408 (4)	0·3016 (2)	0·0774 (18)
C(19)	0·6359 (7)	0·5781 (5)	−0·0695 (2)	0·1003 (23)
C(20)	0·8555 (5)	1·3828 (4)	0·1370 (2)	0·0602 (14)
C(21)	0·9347 (5)	1·4126 (4)	0·1923 (2)	0·0629 (15)
C(22)	1·0046 (5)	1·5266 (4)	0·2009 (2)	0·0664 (15)
C(23)	0·9974 (5)	1·6114 (4)	0·1539 (2)	0·0617 (14)
C(24)	0·9189 (5)	1·5811 (4)	0·0986 (2)	0·0717 (16)
C(25)	0·8467 (5)	1·4681 (4)	0·0904 (2)	0·0714 (16)
C(26)	1·0471 (6)	1·8171 (5)	0·1226 (2)	0·0954 (22)
O(1)	0·9076 (4)	1·2056 (3)	0·0411 (1)	0·0885 (13)
O(2)	0·5398 (4)	0·6353 (3)	−0·0261 (1)	0·0896 (14)
O(3)	1·0688 (3)	1·7222 (3)	0·1674 (1)	0·0767 (12)
(*b*) Compound (II)				
N	0·7656 (5)	0·6424 (1)	0·7363 (2)	0·0508 (10)
O	0·1111 (5)	0·5152 (1)	0·6588 (1)	0·0600 (9)
O(1)	0·7685 (5)	0·6042 (1)	0·8788 (2)	0·0688 (10)
O(2)	−0·1773 (5)	0·3870 (1)	0·8784 (2)	0·0681 (10)
C(1)	0·6886 (7)	0·6018 (2)	0·8036 (2)	0·0525 (12)
C(3)	0·6065 (7)	0·6553 (2)	0·5797 (2)	0·0612 (13)
C(4)	0·4210 (7)	0·6315 (2)	0·5122 (2)	0·0613 (14)
C(5)	0·2431 (7)	0·5842 (2)	0·5460 (2)	0·0659 (15)
C(7)	−0·0215 (7)	0·4522 (2)	0·7723 (2)	0·0543 (13)
C(8)	−0·0028 (7)	0·4288 (2)	0·8571 (2)	0·0537 (13)
C(9)	0·1842 (7)	0·4481 (2)	0·9135 (2)	0·0585 (14)
C(10)	0·3499 (7)	0·4907 (2)	0·8840 (2)	0·0550 (12)
C(11)	0·6162 (6)	0·6313 (2)	0·6600 (2)	0·0519 (12)
C(12)	0·2671 (7)	0·5599 (2)	0·6256 (2)	0·0553 (13)
C(13)	0·1459 (7)	0·4943 (2)	0·7446 (2)	0·0499 (12)
C(14)	0·3367 (6)	0·5151 (2)	0·8001 (2)	0·0480 (11)
C(15)	0·4970 (6)	0·5614 (2)	0·7650 (2)	0·0500 (12)
C(16)	0·4561 (7)	0·5814 (2)	0·6831 (2)	0·0491 (12)
C(17)	0·5560 (9)	0·5984 (2)	0·4393 (3)	0·0870 (18)
C(18)	0·2829 (9)	0·6906 (2)	0·4757 (3)	0·0910 (19)
C(19)	−0·1805 (9)	0·3645 (2)	0·9657 (3)	0·0775 (16)
C(20)	0·9397 (7)	0·6918 (2)	0·7488 (2)	0·0482 (11)
C(21)	1·1397 (7)	0·6811 (2)	0·8035 (2)	0·0520 (12)
C(22)	1·3112 (7)	0·7285 (2)	0·8149 (2)	0·0601 (14)
C(23)	1·2883 (8)	0·7862 (2)	0·7722 (3)	0·0612 (14)
C(24)	1·0855 (8)	0·7976 (2)	0·7203 (3)	0·0650 (14)
C(25)	0·9108 (7)	0·7511 (2)	0·7090 (2)	0·0580 (13)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)
C(1)—N	1·417 (5)	1·418 (4)	C(9)—C(10)	1·374 (6)	1·372 (5)
C(1)—C(15)	1·476 (5)	1·460 (5)	C(10)—C(14)	1·388 (6)	1·386 (5)
C(1)—O(1)	1·211 (5)	1·222 (4)	C(11)—C(16)	1·438 (5)	1·424 (5)
N—C(11)	1·406 (5)	1·424 (5)	C(12)—C(16)	1·415 (5)	1·413 (5)
N—C(20)	1·425 (5)	1·418 (4)	C(13)—C(14)	1·402 (5)	1·399 (5)
C(3)—C(4)	1·519 (5)	1·511 (5)	C(14)—C(15)	1·452 (5)	1·435 (5)
C(3)—C(11)	1·312 (6)	1·331 (5)	C(15)—C(16)	1·329 (5)	1·337 (4)
C(4)—C(5)	1·518 (6)	1·506 (6)	C(19)—O(2)	1·420 (5)	1·424 (5)
C(4)—C(17)	1·537 (6)	1·543 (6)	C(20)—C(21)	1·377 (6)	1·381 (5)
C(4)—C(18)	1·526 (6)	1·540 (6)	C(20)—C(25)	1·383 (6)	1·381 (5)
C(5)—C(12)	1·318 (6)	1·325 (5)	C(21)—C(22)	1·378 (6)	1·377 (5)
O—C(12)	1·393 (4)	1·386 (4)	C(22)—C(23)	1·386 (6)	1·369 (5)
O—C(13)	1·392 (4)	1·395 (4)	C(23)—C(24)	1·378 (6)	1·371 (6)
C(7)—C(8)	1·398 (6)	1·392 (5)	C(24)—C(25)	1·375 (6)	1·375 (6)
C(7)—C(13)	1·374 (5)	1·362 (5)	C(23)—O(3)	1·368 (5)	
C(8)—C(9)	1·387 (6)	1·381 (5)	C(26)—O(3)	1·432 (5)	
C(8)—O(2)	1·354 (5)	1·356 (5)			

	(I)	(II)		(I)	(II)
C(1)—N—C(11)	110·9 (4)	108·7 (3)	O—C13—C14	124·4 (3)	123·3 (3)
C(1)—N—C(20)	124·2 (4)	126·6 (3)	C(7)—C(8)—C(9)	120·8 (3)	120·6 (3)
N—C(1)—C(15)	104·9 (4)	106·6 (3)	C(7)—C(8)—O(2)	114·1 (3)	115·4 (3)
C(1)—C(15)—C(14)	133·9 (4)	133·4 (3)	C(8)—C(7)—C(13)	119·2 (3)	119·8 (3)
C(1)—C(15)—C(16)	107·6 (4)	107·0 (3)	C(7)—C(13)—C(14)	121·0 (3)	121·2 (3)
N—C(1)—O(1)	124·6 (4)	124·0 (3)	C(8)—C(9)—C(10)	118·8 (4)	118·5 (3)
C(15)—C(1)—O(1)	130·5 (4)	129·4 (3)	C(9)—C(8)—O(2)	125·1 (3)	124·1 (3)
N—C(11)—C(3)	134·7 (4)	135·5 (3)	C(8)—O(2)—C(19)	118·4 (3)	118·7 (3)
N—C(11)—C(16)	104·2 (4)	105·0 (3)	C(9)—C(10)—C(14)	122·0 (4)	122·6 (3)
C(11)—N—C(20)	124·7 (4)	126·6 (3)	C(10)—C(14)—C(13)	118·2 (4)	117·4 (3)
N—C(20)—C(21)	120·5 (4)	119·5 (3)	C(10)—C(14)—C(15)	126·5 (4)	126·2 (3)
N—C(20)—C(25)	119·9 (4)	121·4 (3)	C(11)—C(16)—C(12)	120·9 (4)	121·9 (3)
C(3)—C(4)—C(5)	114·1 (4)	114·4 (3)	C(11)—C(16)—C(15)	112·4 (4)	112·4 (3)
C(3)—C(4)—C(17)	107·9 (4)	107·8 (3)	C(12)—C(16)—C(15)	126·5 (4)	125·5 (3)
C(3)—C(4)—C(18)	109·4 (4)	107·6 (3)	C(13)—C(14)—C(15)	115·3 (4)	116·4 (3)
C(4)—C(3)—C(11)	121·2 (4)	120·8 (3)	C(14)—C(15)—C(16)	118·5 (4)	118·9 (3)
C(3)—C(11)—C(16)	121·0 (4)	120·5 (3)	C(20)—C(21)—C(22)	120·2 (5)	119·8 (3)
C(4)—C(5)—C(12)	121·5 (4)	122·0 (3)	C(21)—C(20)—C(25)	119·6 (4)	119·1 (3)
C(5)—C(4)—C(17)	108·6 (4)	108·2 (3)	C(20)—C(25)—C(24)	120·3 (5)	120·2 (3)
C(5)—C(4)—C(18)	107·9 (4)	108·7 (3)	C(21)—C(22)—C(23)	120·1 (5)	121·1 (3)
C(17)—C(4)—C(18)	108·9 (4)	110·0 (3)	C(22)—C(23)—C(24)	119·6 (5)	119·0 (4)
C(5)—C(12)—O	123·5 (3)	124·0 (3)	C(22)—C(23)—O(3)	115·5 (5)	
C(5)—C(12)—C(16)	120·9 (4)	119·8 (3)	C(23)—C(24)—C(25)	120·2 (5)	120·7 (3)
O—C(12)—C(16)	115·6 (3)	116·2 (3)	C(24)—C(23)—O(3)	124·9 (5)	
C(12)—O—C(13)	119·4 (3)	119·8 (3)	C(23)—O(3)—C(26)	117·2 (5)	
O—C(13)—C(7)	114·5 (3)	115·5 (3)			

	(I)	(II)
C(1)—N—C20—C25	53·4 (6)	−138·5 (4)
C(13)—C(14)—C(15)—C(16)	3·5 (5)	−0·2 (5)
C(14)—C(15)—C(16)—C(12)	−4·9 (6)	−1·2 (6)
C(15)—C(16)—C(12)—O	2·0 (6)	1·2 (6)
C(16)—C(12)—O—C(13)	2·2 (5)	0·2 (5)
C(12)—O—C(13)—C(14)	−3·3 (5)	−1·5 (5)
O—C(13)—C(14)—C(15)	0·4 (6)	1·5 (5)
C(3)—C(4)—C(5)—C(12)	7·2 (6)	−7·8 (5)
C(4)—C(5)—C(12)—C(16)	−4·2 (6)	3·9 (6)
C(5)—C(12)—C(16)—C(11)	−1·2 (6)	3·4 (6)
C(12)—C(16)—C(11)—C(3)	3·2 (6)	−6·4 (6)
C(16)—C(11)—C(3)—C(4)	0·3 (6)	1·8 (5)
C(11)—C(3)—C(4)—C(5)	−5·1 (6)	4·9 (5)
C(1)—N—C(11)—C(16)	0·1 (4)	−2·3 (4)
N—C(11)—C(16)—C(15)	1·0 (4)	−0·6 (4)
C(11)—C(16)—C(15)—C(1)	−1·6 (4)	3·1 (4)
C(16)—C(15)—C(1)—N	1·6 (4)	−4·4 (4)
C(15)—C(1)—N—C(11)	−1·0 (4)	4·1 (4)

Discussion. The final atomic coordinates of the two compounds are listed in Tables 1(*a*) and 1(*b*),* respectively, and *PLUTO* (Motherwell & Clegg, 1978) plots of their molecules are shown in Figs. 1(*a*) and 1(*b*). Bond lengths, bond angles and selected torsion angles involving the non-H atoms are listed in Table 2. Figs. 2(*a*) and 2(*b*) show the packing of molecules (I) and (II) in a unit cell.

The corresponding bond lengths and angles in the two compounds are in mutual agreement and are normal. In the heterocycle of the indole ring system, the values of $C_{(sp^2)}$—N distances, C(1)—N [1·417 (4) and 1·418 (4) Å] and C(11)—N [1·406 (5) and 1·424 (5) Å] are not very different from the values reported in 6,6-dimethyl-4-oxo-1,2-diphenyl-4,5,6,7-

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters, bond lengths and angles involving H atoms, intermolecular contacts and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52793 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetrahydroindole (Babu Varghese, Srinivasan, Padmanabhan & Ramadas, 1986) for the same bond.

Conformation. The endocyclic torsion angles of the fused rings are all small showing that the lactam is essentially planar. However, the individual rings exhibit small but differing deviations from planarity, which can be attributed to varying environments caused by differences in substituents and packing. The volume per non-H atom is 16·9 Å^3 in compound (I) while it is smaller, 16·5 Å^3, in compound (II).

While the anisole rings are planar in both compounds, the pyran rings assume distorted boat conformations, the asymmetry parameters of the ring being ΔC_s(O) [1·7 (5)°] and ΔC_s(13) [0·0 (5)°] in compounds (I) and (II), respectively. A similar conformation for the pyran ring has been reported in hexachloroxanthene (Soderholm, Sonnerstam, Norrestam & Palm, 1976).

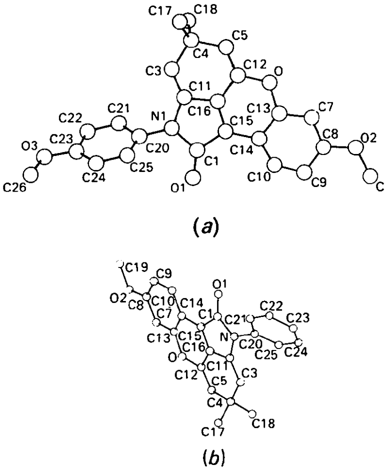

Fig. 1. *PLUTO* plots of the molecules of (*a*) compound (I) and (*b*) compound (II).

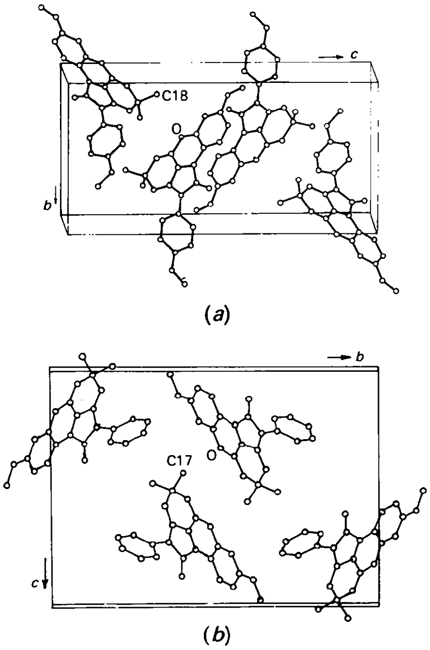

Fig. 2. Packing of the molecules in a unit cell. (*a*) Compound (I); (*b*) compound (II). The pyran ring oxygen O is marked in the figures.

The conformation of the five-membered heterocycle of the indole ring is a distorted envelope in (I) with C(15) at the flap, and a distorted half-chair in (II) with C(1) and C(15) being displaced on either side of the plane formed by the other three atoms.

The phenyl rings in both compounds are planar, but that in (II) has relatively larger scatter in the positions of the atoms from the mean plane of the ring. This ring is rotated from the plane of the five-membered ring C(1)—N—C(11)—C(16)—C(15) about the N—C(20) bond by 53·4 (6)° in (I) and − 138·5 (4)° in (II) so as to avoid short non-bonded interactions between the atoms of this ring and the atoms of the heterocycle [*e.g.* H(3)···H(21) = 2·66 Å in (I), H(3)···H(25) = 2·31 Å in molecule (II)].

The dimethyl substitution has a more significant effect on the conformation of the 1,4-cyclohexadiene, which is known to be planar with D_{2h} symmetry from IR and Raman spectral studies (Dale, 1978). In (I), it assumes a half-chair conformation with C(4) and C(5) displaced, respectively, by − 0·066 and + 0·027 Å from the plane formed by the other four atoms. In (II), however, it assumes a distorted boat conformation with the flag-pole atoms C(4) and C(16) displaced, respectively, by 0·076 and 0·051 Å from the plane formed by the other four atoms.

The intermolecular contacts are van der Waals.

The authors thank the Head, Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras-600 036, for the use of the CAD-4 diffractometer and Dr Babu Varghese, its Senior Scientific Officer, for valuable discussions.

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