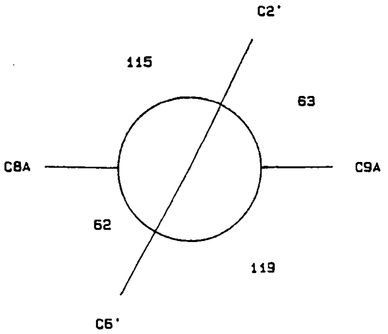

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

bond in Fig. 2. A least-squares plane through the acridinium atoms shows that the acridinium group is not very planar, the maximum distance from the plane being 0·138 Å [C(6)]. The angle between the two least-squares planes through the atoms C(9), N(10), C(1)—C(4), C(4a), C(9a) and C(9), N(10), C(5)—C(8), C(8a), C(10a) is 6·4°. These two planes are planar within 0·018 and 0·035 Å respectively. The phenyl ring is planar within 0·015 Å. The angle between the planes through the acridinium and phenyl groups is 63°.

The O atoms of the crown ether alternate about 0·25 Å above and below their mean plane; the N atom lies 0·88 Å below this plane. For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1·06 Å was obtained. The distance from the Na ion to the centre of gravity of the hetero atoms in the crown ether is 0·83 Å, the angle N(1″)—centre of gravity—Na is 83°.

The Na ion is seven coordinated, with five short distances (about 2·4 Å) to the four O atoms of the crown ether and O(7) of a perchlorate, and two longer distances (about 2·7 Å) to the N atom of the crown ether and O(8) of the same perchlorate. For clarity the two longer distances are not drawn in Fig. 1.

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Crystal Studies of Acridinium Dyes. IX. 10-Methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium Perchlorate

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Abstract. $C_{31}H_{37}N_2O_4^+.ClO_4^-$, $M_r = 601{\cdot}1$, monoclinic, $P2_1/n$, $a = 22{\cdot}332\,(5)$, $b = 13{\cdot}813\,(3)$, $c = 9{\cdot}650\,(3)$ Å, $\beta = 100{\cdot}95\,(3)°$, $V = 2923\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}37$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}81$ cm^{-1}, $F(000) = 1272$, room temperature. Final $R = 0{\cdot}069$ for 2340 observed reflections. The angle between the acridinium and phenyl groups is 78°. Part of the crown ether [C(5″), C(6″), O(7″)] exhibits conformational disorder. There are no unusual bond lengths or angles.

Introduction. The title compound is the ninth structure in a series of acridinium dyes [I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeven (1989); II and IV:

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Table 1. *Fractional coordinates of the non-*H *atoms and equivalent isotropic thermal parameters*

$U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$ (Å^2)
Cl	0·37696 (9)	0·1041 (1)	0·9934 (2)	0·063 (1)
C(1)	0·4985 (3)	0·1542 (5)	0·6729 (7)	0·046 (4)
C(2)	0·5318 (3)	0·0787 (5)	0·7276 (7)	0·055 (4)
C(3)	0·5717 (3)	0·0340 (5)	0·6505 (8)	0·060 (5)
C(4)	0·5756 (3)	0·0636 (5)	0·5206 (8)	0·057 (4)
C(5)	0·5093 (4)	0·2832 (6)	0·1241 (7)	0·059 (5)
C(6)	0·4760 (4)	0·3593 (7)	0·0669 (9)	0·076 (6)
C(7)	0·4364 (4)	0·4074 (6)	0·1436 (9)	0·073 (5)
C(8)	0·4339 (3)	0·3803 (5)	0·2765 (7)	0·054 (4)
C(9)	0·4659 (3)	0·2707 (4)	0·4788 (7)	0·044 (4)
C(11)	0·5746 (4)	0·1162 (6)	0·2294 (9)	0·067 (5)
N(10)	0·5406 (2)	0·1726 (4)	0·3197 (6)	0·043 (3)
O(1)	0·3535 (4)	0·0093 (5)	1·0048 (7)	0·109 (5)
O(2)	0·3784 (4)	0·1558 (6)	1·1175 (8)	0·131 (7)
O(3)	0·3462 (6)	0·1473 (8)	0·880 (1)	0·21 (1)
O(4)	0·4397 (4)	0·0937 (7)	0·984 (1)	0·149 (8)
C(4a)	0·5399 (3)	0·1415 (4)	0·4565 (7)	0·044 (4)
C(8a)	0·4694 (3)	0·3014 (5)	0·3416 (7)	0·044 (4)
C(9a)	0·5000 (3)	0·1897 (5)	0·5356 (6)	0·041 (4)
C(10a)	0·5083 (3)	0·2520 (5)	0·2645 (7)	0·044 (4)
C(2″)	0·3112 (4)	0·5872 (6)	0·7812 (8)	0·071 (5)
C(3″)	0·3376 (4)	0·6145 (6)	0·9287 (8)	0·071 (5)
C(5a″)	0·3697 (8)	0·769 (1)	1·064 (2)	0·072 (4)†
(C5b″)	0·3360 (8)	0·746 (1)	1·068 (2)	0·067 (4)†
C(6a″)	0·3449 (7)	0·741 (1)	1·195 (2)	0·058 (4)†
C(6b″)	0·3774 (8)	0·697 (1)	1·182 (2)	0·078 (5)†
C(8″)	0·3614 (4)	0·6428 (7)	1·4016 (8)	0·075 (6)
C(9″)	0·3038 (4)	0·5875 (6)	1·3790 (7)	0·062 (5)
C(11″)	0·2558 (4)	0·4503 (7)	1·2617 (8)	0·074 (5)
C(12″)	0·2586 (4)	0·3819 (6)	1·1446 (8)	0·074 (6)
C(14″)	0·2487 (3)	0·3771 (5)	0·8942 (7)	0·056 (4)
C(15″)	0·2463 (3)	0·4413 (5)	0·7704 (7)	0·053 (4)
N(1″)	0·3044 (3)	0·4839 (4)	0·7557 (6)	0·054 (4)
O(4″)	0·3388 (3)	0·7178 (3)	0·9347 (5)	0·063 (3)
O(7a″)	0·3812 (5)	0·6612 (7)	1·260 (1)	0·060 (3)†
O(7b″)	0·3662 (6)	0·7258 (9)	1·314 (1)	0·084 (3)†
O(10″)	0·3067 (2)	0·5112 (4)	1·2824 (5)	0·067 (3)
O(13″)	0·2502 (2)	0·4349 (4)	1·0162 (5)	0·063 (3)
C(1′)	0·4247 (3)	0·3218 (5)	0·5595 (7)	0·043 (4)
C(2′)	0·3680 (3)	0·2840 (4)	0·5716 (7)	0·046 (4)
C(3′)	0·3305 (3)	0·3382 (5)	0·6393 (7)	0·047 (4)
C(4′)	0·3454 (3)	0·4295 (4)	0·6975 (6)	0·042 (4)
C(5′)	0·4039 (3)	0·4640 (5)	0·6879 (7)	0·055 (4)
C(6′)	0·4418 (3)	0·4106 (5)	0·6213 (7)	0·051 (4)
C(7′)	0·3469 (4)	0·1866 (5)	0·5097 (9)	0·069 (5)

† Refined isotropically.

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

Cl—O(1)	1·422 (7)	C(8a)—C(10a)	1·421 (10)
Cl—O(2)	1·389 (8)	O(7a″)—C(8″)	1·54 (1)
Cl—O(3)	1·32 (1)	C(5b″)—C(6b″)	1·46 (2)
Cl—O(4)	1·428 (9)	C(5b″)—O(4″)	1·36 (2)
C(1)—C(2)	1·330 (9)	C(6b″)—O(7b″)	1·40 (2)
C(1)—C(9a)	1·419 (9)	O(7b″)—C(8″)	1·44 (2)
C(2)—C(3)	1·41 (1)	C(2″)—C(3″)	1·48 (1)
C(3)—C(4)	1·34 (1)	C(2″)—N(1″)	1·451 (10)
C(4)—C(4a)	1·410 (9)	C(3″)—O(4″)	1·428 (9)
C(5)—C(6)	1·34 (1)	C(8″)—C(9″)	1·48 (1)
C(5)—C(10a)	1·426 (10)	C(9″)—O(10″)	1·417 (9)
C(6)—C(7)	1·42 (1)	C(11″)—C(12″)	1·48 (1)
C(7)—C(8)	1·35 (1)	C(11″)—O(10″)	1·40 (1)
C(8)—C(8a)	1·422 (9)	C(12″)—O(13″)	1·421 (10)
C(9)—C(8a)	1·406 (9)	C(14″)—C(15″)	1·48 (1)
C(9)—C(9a)	1·405 (9)	C(14″)—O(13″)	1·418 (9)
C(9)—C(1′)	1·491 (10)	C(15″)—N(1″)	1·456 (10)
C(11)—N(10)	1·48 (1)	N(1″)—C(4′)	1·383 (9)
N(10)—C(4a)	1·391 (9)	C(1′)—C(2′)	1·395 (10)
N(10)—C(10a)	1·364 (8)	C(1′)—C(6′)	1·385 (9)
C(4a)—C(9a)	1·442 (10)	C(2′)—C(3′)	1·377 (10)
C(5a″)—C(6a″)	1·52 (2)	C(2′)—C(7′)	1·511 (10)
C(5″)—O(4″)	1·49 (2)	C(3′)—C(4′)	1·395 (9)
C(6″)—O(7a″)	1·44 (2)	C(4′)—C(5′)	1·41 (1)
		C(5′)—C(6′)	1·37 (1)

O(1)—Cl—O(2)	110·8 (5)	N(10)—C(10a)—C(8a)	120·8 (6)
O(1)—Cl—O(3)	109·8 (6)	C(6a″)—O(7a″)—C(8″)	106·3 (10)
O(1)—Cl—O(4)	107·0 (5)	C(6b″)—C(5b″)—O(4″)	116 (1)
O(2)—Cl—O(3)	113·9 (6)	C(5b″)—C(6b″)—O(7b″)	111 (1)
O(2)—Cl—O(4)	104·1 (6)	C(6b″)—O(7b″)—C(8″)	111 (1)
O(3)—Cl—O(4)	110.8 (7)	C(3″)—C(2″)—N(1″)	115·0 (6)
C(2)—C(1)—C(9a)	122·1 (7)	C(2″)—C(3″)—O(4″)	107·1 (6)
C(1)—C(2)—C(3)	119·8 (7)	O(7a″)—C(8″)—C(9″)	110·1 (7)
C(2)—C(3)—C(4)	121·5 (7)	O(7b″)—C(8″)—C(9″)	119·0 (8)
C(3)—C(4)—C(4a)	120·8 (7)	C(8″)—C(9″)—O(10″)	109·6 (7)
C(6)—C(5)—C(10a)	121·3 (8)	C(12″)—C(11″)—O(10″)	110·0 (7)
C(5)—C(6)—C(7)	120·1 (8)	C(11″)—C(12″)—O(13″)	108·6 (7)
C(6)—C(7)—C(8;	120·5 (7)	C(15″)—C(14″)—O(13″)	108·9 (6)
C(7)—C(8)—C(8a)	120·9 (7)	C(14″)—C(15″)—N(1″)	115·1 (5)
C(8a)—C(9)—C(9a)	119·0 (6)	C(2″)—N(1″)—C(15″)	116·6 (6)
C(8a)—C(9)—C(1′)	119·9 (5)	C(2″)—N(1″)—C(4′)	123·2 (6)
C(9a)—C(9)—C(1′)	121·0 (6)	C(15″)—N(1″)—C(4′)	119·4 (5)
C(11)—N(10)—C(4a)	119·7 (5)	C(5a″)—O(4″)—C(3″)	120·8 (8)
C(11)—N(10)—C(10a)	119·0 (6)	C(5b″)—O(4″)—C(3″)	108·7 (8)
C(4a)—N(10)—C(10a)	121·2 (6)	C(9″)—O(10″)—C(11″)	113·8 (6)
C(4)—C(4a)—N(10)	123·0 (6)	C(12″)—O(13″)—C(14″)	114·4 (6)
C(4)—C(4a)—C(9a)	118·4 (6)	C(9)—C(1′)—C(2′)	121·8 (6)
N(10)—C(4a)—C(9a)	118·6 (5)	C(9)—C(1′)—C(6′)	119·8 (6)
C(6a″)—C(5a″)—O(4″)	113 (1)	C(2′)—C(1′)—C(6′)	118·4 (6)
C(5a″)—C(6a″)—O(7a″)	107 (1)	C(1′)—C(2′)—C(3′)	118·7 (6)
C(8)—C(8a)—C(9)	121·4 (6)	C(1′)—C(2′)—C(7′)	121·3 (6)
C(8)—C(8a)—C(10a)	118·8 (6)	C(3′)—C(2′)—C(7′)	120·0 (6)
C(9)—C(8a)—C(10a)	119·8 (6)	C(2′)—C(3′)—C(4′)	124·2 (6)
C(1)—C(9a)—C(9)	122·2 (6)	N(1″)—C(4′)—C(3′)	121·9 (6)
C(1)—C(9a)—C(4a)	117·5 (6)	N(1″)—C(4′)—C(5′)	122·4 (6)
C(9)—C(9a)—C(4a)	120·3 (6)	C(3′)—C(4′)—C(5′)	115·6 (6)
C(5)—C(10a)—N(10)	120·8 (6)	C(4′)—C(5′)—C(6′)	120·7 (6)
C(5)—C(10a)—C(8a)	118·3 (6)	C(1′)—C(6′)—C(5′)	122·3 (7)

Reiss, Goubitz & Heijdenrijk (1989*a*,*b*); III: Kronenburg, Goubitz, Reiss & Heijdenrijk (1989); V and VIII: Goubitz, Reiss & Heijdenrijk (1989*a*,*b*); VI: Zoutberg, Reiss, Goubitz & Heijdenrijk (1989); VII: Kronenburg, Reiss, Goubitz & Heijdenrijk (1989)]. In this case the phenyl ring is substituted with methyl and aza-15-crown-5 groups. Disorder is found in the crown ether.

Experimental. A dark-violet plate-shaped crystal (dimensions 0·13 × 0·50 × 0·50 mm approximately) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation and θ–2θ scan. A total of 5101 unique reflections was measured within the range $-26 \leq h \leq 25$, $0 \leq k \leq 16$, $0 \leq l \leq 11$. Of these, 2340 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·59 Å^{-1}. Two standard reflections (620, $\bar{3}22$) were measured hourly, the intensity decrease was about 12% during the 57 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $30 < 2\theta < 37°$. Corrections for Lorentz and polarization effects were applied. The structure was determined by direct methods using the program *SAPI* (Yao Jia-xing, Zheng Chao-de, Qian Jin-zi, Han Fu-son, Gu Yuan-xin & Fan Hai-fu, 1985). After isotropic refinement it was found that the atoms C(5″), C(6″) and O(7″) of the crown ether possessed very high thermal parameters and had distances and angles which differ appreciably from the normal values. The electron-density distributions associated with these atoms appeared to be very broad exhibiting two maxima. This was taken as an indication of conformational disorder. Therefore, two conformations for the crown-ether moiety were assumed and in the subsequent refinement two half atoms were introduced for each of the three atoms. Refinement of the population parameters of these atoms gave no significant improvement, so it was decided to fix these parameters at a value of 0·5. The positions of the H atoms were calculated, except those of the disordered atoms which were ignored. Block-diagonal least-squares refinement on F, isotropic for the disordered atoms and the H atoms and anisotropic for the remaining non-H atoms, converged to $R = 0{\cdot}069$, $wR = 0{\cdot}105$, $(\Delta/\sigma)_{\max} = 0{\cdot}63$. A weighting scheme $w = (4{\cdot}86 + F_{\rm obs} + 0{\cdot}016F_{\rm obs}^2)^{-1}$ was used. An empirical absorption correction was applied, with corrections in the range 0·66–1·42 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between −0·2 and 0·3 e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Cl was corrected for. All calculations were performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), unless stated otherwise.*

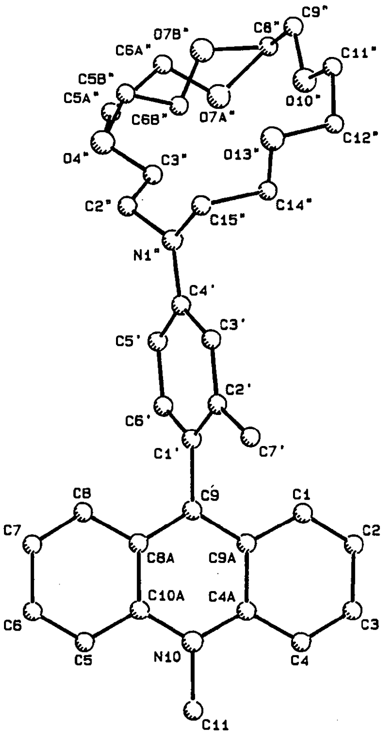

Fig. 1. Structure of $[C_{31}N_2O_4]^+$ showing the numbering scheme.

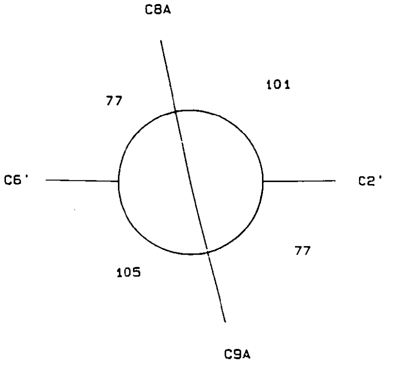

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

Discussion. Final positional parameters for the non-H atoms are listed in Table 1, bond lengths and bond angles in Table 2. A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule is given in Fig. 1 and the Newman projection along the C(9)—C(1′) bond in Fig. 2. A least-squares plane through the acridinium atoms shows that the acridinium group is planar, the maximum distance from the plane being 0·034 Å. The phenyl ring is planar within 0·013 Å. The angle between the planes through the acridinium and phenyl groups is 78°. The O atoms of conformation *A* alternate about 0·14 Å above and below their mean plane; the N atom lies 1·52 Å above this plane. For conformation *B* the values obtained are 0·09 and 1·13 Å respectively. A mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), has been calculated using the centre of gravity of the O and N atoms instead of the metal-ion position. In this way a value of 1·15 Å for *A* and 1·30 Å for *B* was obtained.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as supplementary Publication No. SUP 51853 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of (±)-*cis*-2-Hydroxy-4-(2-phenylethyl)- (I) and *cis*-4-Phenyl-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (II)

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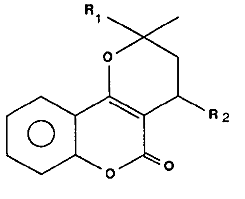
Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (I) Racemic *cis*-2-hydroxy-4-(2-phenylethyl), $C_{21}H_{20}O_4$, $M_r = 336{\cdot}39$, triclinic, $P\bar{1}$, $a = 8{\cdot}660\,(7)$, $b = 14{\cdot}299\,(4)$, $c = 7{\cdot}320\,(4)$ Å, $\alpha = 96{\cdot}68\,(3)$, $\beta = 99{\cdot}07\,(5)$, $\gamma = 87{\cdot}554\,(4)°$, $V = 888{\cdot}8\,(16)$ Å^3, $Z = 2$, $D_x = 1{\cdot}257$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71078$ Å, $\mu = 0{\cdot}807$ cm^{-1}, $F(000) = 354$, $T = 294$ K, final $R = 0{\cdot}045$ for 2844 observations $[I \geq 3\sigma(I)]$. Molecules are hydrogen bonded between hydroxyls and coumarin carbonyl groups in chains along **c**, with O···O separation of 2·772 (2) Å. The dihydropyran ring is a half-chair, $\Delta C_2 = 0{\cdot}0057\,(8)$. (II) Spontaneously resolved *cis*-4-phenyl, $C_{19}H_{16}O_3$, $M_r = 292{\cdot}34$, monoclinic, $P2_1$, $a = 8{\cdot}267\,(6)$, $b = 10{\cdot}699\,(7)$, $c = 9{\cdot}039\,(6)$ Å, $\beta = 113{\cdot}67\,(6)°$, $V = 732{\cdot}2\,(18)$ Å^3, $Z = 2$, $D_x = 1{\cdot}326$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71078$ Å, $\mu = 0{\cdot}831$ cm^{-1}, $F(000) = 308$, $T = 294$ K, final $R = 0{\cdot}061$ for 2149 observations $[I \geq 2\sigma(I)]$. The dihydropyran ring is in the *d,e*-diplanar conformation, $\Delta C_2 = 0{\cdot}0569\,(13)$, and retains the relatively long C—O bond, 1·474 (2) Å, compared to its 2-hydroxy derivatives.

Introduction. Dihydropyran-ring shape near the low-energy conformation can be studied through the molecular structures of a series of crystalline warfarin derivatives containing the embedded heterocycle. Warfarin (R_1 = OH, R_2 = phenyl) crystallizes as the hemiketal while in solution it exists as a mixture of diastereomeric hemiketals and an intermediate keto form. This contribution describes the structures of two analogs: one in which the phenyl has a short intervening alkyl chain (I), and another which lacks the hemiketal oxygen (II).



(I) R_1 = OH $R_2 = CH_2CH_2C_6H_5$
(II) R_1 = H $R_2 = C_6H_5$

The latter compound is examined for comparison with the many 4-substituted 2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-ones already studied. This molecule does not undergo solution equilibrium between configurational isomers, lacks the operative anomeric effect, and does not form intermolecular hydrogen bonds as do warfarin hemiketals. Consequently the embedded dihydropyran ring in (II) has fewer influences upon it.

Experimental. The Michael-type addition of *α,β*-unsaturated ketones to 4-hydroxycoumarin is a useful path to a variety of warfarin analogs (Ikawa, Stahmann & Link, 1944). Thus 6-phenyl-3-buten-2-one produces (I) on formation of the cyclic

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