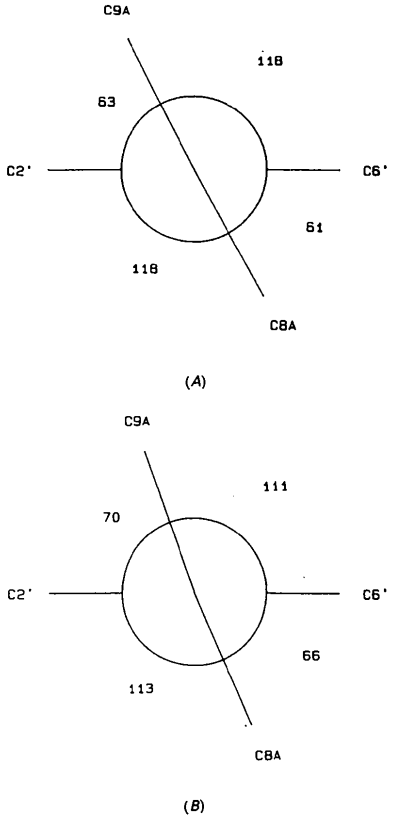

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

Table 1. Bond lengths and bond angles are listed in Table 2. A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule (*A*) is given in Fig. 1 [(*B*) is very similar] and the Newman projections along the C(9)—C(1′) bond for (*A*) and (*B*) are depicted in Fig. 2. A least-squares plane through the acridinium atoms of (*A*) shows that the maximum distance from the plane is 0·104 Å. The phenyl ring of (*A*) is planar within 0·008 Å. The angle between the two planes of (*A*) is 63°. A least-squares plane through the acridinium atoms of (*B*) shows that the acridinium is less planar than in (*A*). The four outermost atoms of the acridinium (*B*), [C(2), C(3), C(6), C(7)], are bent upwards out of the plane. The maximum distance from the plane is 0·189 Å. The phenyl ring is planar within 0·018 Å. The angle between the two planes of (*B*) is 70°. Thus, the twist angle between the acridinium and the phenyl planes apparently is not a strict molecular feature, but is sensitive to relatively small energy effects due to differences in packing.

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

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Abstract. $C_{30}H_{35}N_2O_4^+.ClO_4^-$, $M_r = 587{\cdot}1$, monoclinic, $P2_1/n$, $a = 23{\cdot}639\ (1)$, $b = 12{\cdot}659\ (1)$, $c = 9{\cdot}740\ (1)$ Å, $\beta = 90{\cdot}316\ (6)°$, $V = 2914{\cdot}6\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 16{\cdot}0$ cm^{-1}, $F(000) = 1144$, room temperature. Final $R = 0{\cdot}066$ for 3249 observed reflections. The acridinium and phenyl groups are each planar. The angle between the acridinium and phenyl groups is 57°. The mean cavity radius, calculated using the centre of gravity of the O and N atoms, is 1·15 Å.

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

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

	x	y	z	U_{eq}(Å^2)
Cl	0·13278 (5)	0·21298 (9)	0·5764 (1)	0·0600 (6)
C(1)	−0·0177 (2)	0·4174 (3)	0·1403 (4)	0·046 (2)
C(2)	0·0384 (2)	0·4182 (4)	0·1680 (4)	0·055 (2)
C(3)	0·0629 (2)	0·3327 (4)	0·2387 (4)	0·059 (3)
C(4)	0·0304 (2)	0·2490 (4)	0·2791 (4)	0·055 (2)
C(5)	−0·1487 (2)	0·0660 (3)	0·2961 (5)	0·059 (3)
C(6)	−0·2045 (2)	0·0611 (3)	0·2629 (5)	0·061 (3)
C(7)	−0·2322 (2)	0·1427 (3)	0·1947 (5)	0·053 (2)
C(8)	−0·2023 (1)	0·2304 (3)	0·1578 (4)	0·041 (2)
C(9)	−0·1118 (1)	0·3303 (3)	0·1469 (3)	0·034 (2)
C(11)	−0·0347 (2)	0·0776 (4)	0·3769 (6)	0·080 (3)
N(10)	−0·0606 (1)	0·1622 (3)	0·2900 (3)	0·046 (2)
O(1)	0·0859 (2)	0·1496 (3)	0·5530 (5)	0·116 (3)
O(2)	0·1198 (3)	0·3193 (3)	0·5697 (7)	0·157 (5)
O(3)	0·1606 (2)	0·1897 (3)	0·6979 (5)	0·121 (4)
O(4)	0·1695 (3)	0·1903 (9)	0·4745 (8)	0·243 (9)
C(4a)	−0·0279 (2)	0·2468 (3)	0·2510 (4)	0·041 (2)
C(8a)	−0·1437 (1)	0·2392 (3)	0·1833 (4)	0·037 (2)
C(9a)	−0·0539 (1)	0·3327 (3)	0·1800 (3)	0·038 (2)
C(10a)	−0·1165 (1)	0·1559 (3)	0·2570 (4)	0·042 (2)
C(2″)	−0·2012 (2)	0·7815 (3)	−0·1084 (5)	0·058 (3)
C(3″)	−0·2401 (2)	0·8376 (4)	−0·0111 (5)	0·067 (3)
C(5″)	−0·3306 (2)	0·9147 (5)	0·0070 (5)	0·081 (4)
C(6″)	−0·3864 (2)	0·9207 (5)	−0·0597 (7)	0·086 (4)
C(8″)	−0·4678 (3)	0·8198 (6)	−0·1087 (8)	0·109 (5)
C(9″)	−0·4652 (3)	0·7727 (6)	−0·2472 (7)	0·107 (5)
C(11″)	−0·4340 (2)	0·6142 (6)	−0·3636 (7)	0·102 (5)
C(12″)	−0·3878 (3)	0·5334 (5)	−0·3461 (7)	0·098 (4)
C(14″)	−0·3092 (2)	0·6097 (4)	−0·2277 (5)	0·062 (3)
C(15″)	−0·2505 (2)	0·6511 (4)	−0·2613 (4)	0·055 (2)
N(1″)	−0·2158 (1)	0·6720 (3)	−0·1405 (3)	0·049 (2)
O(4″)	−0·2936 (1)	0·8523 (2)	−0·0759 (3)	0·063 (2)
O(7″)	−0·4150 (2)	0·8248 (4)	−0·0358 (5)	0·107 (3)
O(10″)	−0·4409 (2)	0·6664 (4)	−0·2339 (4)	0·098 (3)
O(13″)	−0·3334 (1)	0·5791 (4)	−0·3542 (4)	0·087 (3)
C(1′)	−0·1395 (1)	0·4187 (3)	0·0744 (3)	0·036 (2)
C(2′)	−0·1372 (2)	0·5223 (3)	0·1249 (4)	0·040 (2)
C(3′)	−0·1631 (2)	0·6048 (3)	0·0569 (4)	0·042 (2)
C(4′)	−0·1919 (1)	0·5896 (3)	−0·0684 (4)	0·039 (2)
C(5′)	−0·1946 (2)	0·4850 (3)	−0·1186 (4)	0·042 (2)
C(6′)	−0·1686 (1)	0·4033 (3)	−0·0484 (4)	0·038 (2)

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

Cl—O(1)	1·386 (4)	C(2″)—C(3″)	1·503 (7)
Cl—O(2)	1·382 (5)	C(2″)—N(1″)	1·462 (5)
Cl—O(3)	1·382 (5)	C(3″)—O(4″)	1·423 (6)
Cl—O(4)	1·353 (8)	C(5″)—C(6″)	1·469 (8)
C(1)—C(2)	1·352 (5)	C(5″)—O(4″)	1·431 (6)
C(1)—C(9a)	1·427 (5)	C(6″)—O(7″)	1·410 (7)
C(2)—C(3)	1·406 (6)	C(8″)—C(9″)	1·48 (1)
C(3)—C(4)	1·368 (6)	C(8″)—O(7″)	1·434 (8)
C(4)—C(4a)	1·404 (5)	C(9″)—O(10″)	1·469 (9)
C(5)—C(6)	1·358 (6)	C(11″)—C(12″)	1·505 (9)
C(5)—C(10a)	1·422 (6)	C(11″)—O(10″)	1·436 (8)
C(6)—C(7)	1·390 (6)	C(12″)—O(13″)	1·413 (7)
C(7)—C(8)	1·365 (6)	C(14″)—C(15″)	1·521 (6)
C(8)—C(8a)	1·410 (5)	C(14″)—O(13″)	1·410 (6)
C(9)—C(8a)	1·424 (5)	C(15″)—N(1″)	1·455 (5)
C(9)—C(9a)	1·405 (5)	N(1′)—C(4′)	1·377 (5)
C(9)—C(1′)	1·475 (5)	C(1′)—C(2′)	1·402 (5)
C(11)—N(10)	1·494 (6)	C(1′)—C(6′)	1·390 (5)
N(10)—C(4a)	1·376 (5)	C(2′)—C(3′)	1·378 (5)
N(10)—C(10a)	1·361 (5)	C(3′)—C(4′)	1·407 (5)
C(4a)—C(9a)	1·426 (5)	C(4′)—C(5′)	1·413 (5)
C(8a)—C(10a)	1·427 (5)	C(5′)—C(6′)	1·382 (5)

O(1)—Cl—O(2)	112·3 (4)	C(5)—C(10a)—C(8a)	119·1 (3)
O(1)—Cl—O(3)	113·2 (4)	N(10)—C(10a)—C(8a)	120·7 (3)
O(1)—Cl—O(4)	105·8 (6)	C(3″)—C(2″)—N(1″)	116·0 (3)
O(2)—Cl—O(3)	110·6 (4)	C(2″)—C(3″)—O(4″)	109·1 (3)
O(2)—Cl—O(4)	108·4 (7)	C(6″)—C(5″)—O(4″)	109·2 (4)
O(3)—Cl—O(4)	106·2 (6)	C(5″)—C(6″)—O(7″)	108·2 (4)
C(2)—C(1)—C(9a)	122·7 (3)	C(9″)—C(8″)—O(7″)	115·5 (5)
C(1)—C(2)—C(3)	119·5 (4)	C(8″)—C(9″)—O(10″)	107·9 (5)
C(2)—C(3)—C(4)	120·4 (4)	C(12″)—C(11″)—O(10″)	107·4 (5)
C(3)—C(4)—C(4a)	120·8 (4)	C(11″)—C(12″)—O(13″)	112·1 (4)
C(6)—C(5)—C(10a)	119·6 (4)	C(15″)—C(14″)—O(13″)	105·8 (3)
C(5)—C(6)—C(7)	122·3 (4)	C(14″)—C(15″)—N(1″)	113·6 (3)
C(6)—C(7)—C(8)	119·1 (4)	C(2″)—N(1″)—C(15″)	118·5 (5)
C(7)—C(8)—C(8a)	121·8 (3)	C(2″)—N(1″)—C(4′)	120·9 (3)
C(8a)—C(9)—C(9a)	118·5 (3)	C(15″)—N(1″)—C(4′)	120·2 (3)
C(8a)—C(9)—C(1′)	120·0 (3)	C(3″)—O(4″)—C(5″)	111·5 (4)
C(9a)—C(9)—C(1′)	121·5 (3)	C(6″)—O(7″)—C(8″)	111·9 (6)
C(11)—N(10)—C(4a)	119·0 (4)	C(9″)—O(10″)—C(11″)	113·0 (6)
C(11)—N(10)—C(10a)	119·1 (4)	C(12″)—O(13″)—C(14″)	115·4 (4)
C(4a)—N(10)—C(10a)	121·8 (3)	C(9)—C(1′)—C(2′)	121·7 (3)
C(4)—C(4a)—N(10)	120·9 (3)	C(9)—C(1′)—C(6′)	121·5 (3)
C(4)—C(4a)—C(9a)	120·0 (3)	C(2′)—C(1′)—C(6′)	116·8 (3)
N(10)—C(4a)—C(9a)	119·1 (3)	C(1′)—C(2′)—C(3′)	121·6 (3)
C(8)—C(8a)—C(9)	122·8 (3)	C(2′)—C(3′)—C(4′)	121·6 (3)
C(8)—C(8a)—C(10a)	118·0 (3)	N(1′)—C(4′)—C(3′)	122·3 (3)
C(9)—C(8a)—C(10a)	119·1 (3)	N(1′)—C(4′)—C(5′)	121·1 (3)
C(1)—C(9a)—C(9)	122·6 (3)	C(3′)—C(4′)—C(5′)	116·7 (3)
C(1)—C(9a)—C(4a)	116·5 (3)	C(4′)—C(5′)—C(6′)	120·7 (3)
C(9)—C(9a)—C(4a)	120·8 (3)	C(1′)—C(6′)—C(5′)	122·5 (3)
C(5)—C(10a)—N(10)	120·3 (3)		

Introduction. The title compound is the fifth structure in a series of acridinium dyes [I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeven (1989); II and IV: Reiss, Goubitz & Heijdenrijk (1989*a*,*b*); III: Kronenburg, Goubitz, Reiss & Heijdenrijk (1989)]. In this case the phenyl ring is substituted with an aza-15-crown-5 group. This crown-ether group can form complexes with metal ions leading to remarkable shifts in light absorption (Jonker, Ariese & Verhoeven, 1989). A number of these will be the subject of subsequent papers. Relations between structural and photophysical properties of these crown-ether dyes will be discussed in a separate paper (Jonker, Verhoeven, Reiss & Goubitz, 1989).

Experimental. A violet-bronze plate-shaped crystal (dimensions 0·20 × 0·38 × 0·40 mm approximately) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation and θ–2θ scan. A total of 4300 unique reflections was measured within the range $-26 \le h \le 26$, $0 \le k \le 14$, $0 \le l \le 10$. Of these, 3249 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·56 Å^{-1}. Two standard reflections (021, 520) were measured hourly, no significant decrease was measured during the 48 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $70 < 2\theta < 80°$. Corrections for Lorentz and polarization effects were applied. The structure was determined by direct methods using the program *SIMPEL* (Schenk & Kiers, 1985). From a ΔF synthesis the H atoms were derived. Block-diagonal least-squares refinement on F, anisotropic for the non-H atoms and isotropic for the H atoms converged to $R = 0{\cdot}066$, $wR = 0{\cdot}090$, $(\Delta/\sigma)_{max} = 0{\cdot}19$. A weighting scheme $w = (6{\cdot}84 + F_{obs} + 0{\cdot}006F_{obs}^2)^{-1}$ was used. The isotropic secondary-extinction coefficient refined to $5\,(1) \times 10^{-4}$ (Zachariasen, 1968). An empirical absorption correction was applied, with corrections in the range 0·80–1·21 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density

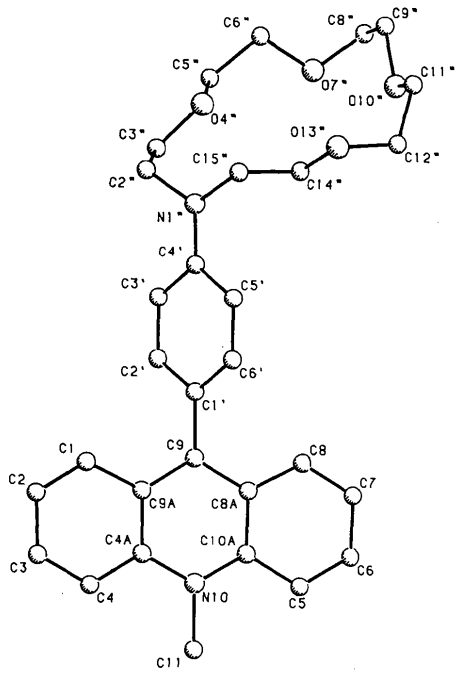

Fig. 1. Structure of $[C_{30}H_{35}N_2O_4]^+$ showing the numbering scheme.

between $-0{\cdot}2$ and $0{\cdot}5$ 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 *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), unless stated otherwise.*

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 nearly planar, the maximum distance from the plane is 0·050 Å. The phenyl ring is planar within 0·010 Å. The angle between the two planes is 57°.

* 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 51849 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

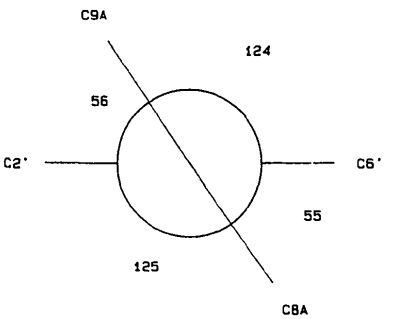

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

The O atoms of the crown ether form an almost planar tetragon, alternately about 0·08 Å above and below their mean plane; the N atom lies 1·189 Å below this plane. 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 radius of 1·15 Å is obtained.

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