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

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Abstract. $C_{30}H_{35}N_2O_4^+.Na^+.2ClO_4^-$, $M_r = 709·5$, triclinic, $P\overline{1}$, $a = 14·510\ (2)$, $b = 14·720\ (3)$, $c = 8·559\ (1)$ Å, $\alpha = 105·82\ (1)$, $\beta = 94·15\ (1)$, $\gamma = 83·07\ (1)°$, $V = 1744·5\ (6)$ Å^3, $Z = 2$, $D_x = 1·35$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·5418$ Å, $\mu = 23·4$ cm^{-1}, $F(000) = 740$, room temperature. Final $R = 0·078$ for 1847 observed reflections. The angle between the acridinium and phenyl groups is 63°. The mean cavity radius of the crown ether is 1·06 Å. The Na atom is seven coordinated by six O atoms and one N atom, with five short and two longer distances (about 2·4 and 2·7 Å, respectively).

Introduction. The title compound is the eighth 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); V: Goubitz, Reiss & Heijdenrijk (1989); VI: Zoutberg, Reiss, Goubitz & Heijdenrijk (1989); VII: Kronenburg, Reiss, Goubitz & Heijdenrijk (1989)]. In this case the phenyl ring is substituted with an aza-15-crown-5 group, which has formed a complex with sodium diperchlorate.

Experimental. A yellow-orange plate-shaped crystal (dimensions $0·13 \times 0·33 \times 0·38$ 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 2803 unique reflections was measured within the range $-13 \le h \le 13$, $-13 \le k \le 13$, $0 \le l \le 7$. Of these, 1847 were above the significance level of $2·5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·46 Å^{-1}. Two standard reflections ($2\overline{2}1$, $\overline{3}\overline{2}1$) were measured hourly, no significant decrease was measured during the 31 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $40 < 2\theta < 50°$. 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, a ΔF synthesis revealed two peaks of heights 3·8 and 2·9 e Å^{-3} at a distance of about 2 Å, which might be taken as an indication of the presence of a solvent molecule. Although 2 Å does not agree with the C—O distance in methanol, one of the solvents used in the crystallization process, we have, lacking an alternative interpretation, assigned C and O atoms to the peaks and included these in the anisotropic

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

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

	x	y	z	U_{eq}(Å^2)
Na	0·8397 (3)	−0·3090 (3)	1·0205 (5)	0·049 (3)
Cl(1)	0·8180 (2)	0·2028 (2)	0·4564 (4)	0·063 (2)
Cl(2)	0·6451 (2)	−0·2676 (2)	0·8550 (4)	0·062 (2)
C(1)	0·6741 (8)	−0·0661 (8)	0·504 (1)	0·045 (7)
C(2)	0·6414 (8)	−0·1021 (9)	0·349 (1)	0·051 (8)
C(3)	0·5824 (8)	−0·0444 (9)	0·273 (1)	0·053 (8)
C(4)	0·5577 (8)	0·0501 (8)	0·345 (1)	0·048 (8)
C(5)	0·5533 (8)	0·3118 (8)	0·829 (1)	0·052 (8)
C(6)	0·5787 (9)	0·3457 (9)	0·989 (1)	0·061 (9)
C(7)	0·6488 (10)	0·2939 (9)	1·070 (1)	0·063 (9)
C(8)	0·6799 (8)	0·2067 (8)	0·992 (1)	0·047 (8)
C(9)	0·6854 (7)	0·0697 (8)	0·749 (1)	0·038 (8)
C(11)	0·5076 (9)	0·2426 (9)	0·492 (1)	0·063 (9)
N(10)	0·5647 (6)	0·1815 (6)	0·5848 (10)	0·038 (6)
O(1)	0·8200 (10)	0·190 (2)	0·608 (2)	0·23 (2)
O(2)	0·8568 (8)	0·2888 (9)	0·478 (2)	0·12 (1)
O(3)	0·7270 (6)	0·2092 (9)	0·392 (1)	0·103 (8)
O(4)	0·877 (10)	0·139 (1)	0·355 (2)	0·21 (2)
O(5)	0·5892 (7)	−0·3431 (7)	0·777 (1)	0·086 (7)
O(6)	0·5925 (7)	−0·1773 (7)	0·870 (1)	0·088 (7)
O(7)	0·6750 (6)	−0·2749 (7)	1·0170 (10)	0·076 (6)
O(8)	0·7270 (8)	−0·2749 (8)	0·769 (1)	0·102 (8)
C(4a)	0·5899 (7)	0·0878 (7)	0·505 (1)	0·037 (7)
C(8a)	0·6526 (7)	0·1633 (7)	0·827 (1)	0·037 (7)
C(9a)	0·6518 (7)	0·0322 (7)	0·586 (1)	0·039 (7)
C(10a)	0·5882 (7)	0·2189 (7)	0·749 (1)	0·040 (7)
C(s)	0·663 (1)	0·461 (1)	0·580 (2)	0·10 (1)
O(s)	0·5959 (8)	0·5112 (7)	0·390 (2)	0·153 (10)
C(2″)	1·0269 (8)	−0·2004 (8)	0·995 (1)	0·047 (8)
C(3″)	1·0185 (8)	−0·2795 (9)	0·842 (1)	0·054 (8)
C(5″)	0·9599 (9)	−0·4301 (9)	0·729 (1)	0·064 (9)
C(6″)	0·9295 (9)	−0·5104 (9)	0·778 (2)	0·065 (9)
C(8″)	0·8196 (9)	−0·5424 (9)	0·947 (2)	0·068 (10)
C(9″)	0·7660 (9)	−0·4895 (9)	1·092 (2)	0·066 (9)
C(11″)	0·7832 (9)	−0·3610 (9)	1·334 (2)	0·062 (9)
C(12″)	1·8519 (9)	−0·2931 (8)	1·411 (1)	0·055 (8)
C(14″)	0·9479 (8)	−0·1919 (9)	1·338 (1)	0·049 (8)
C(15″)	0·9457 (8)	−0·1187 (8)	1·246 (1)	0·050 (8)
N(1″)	0·9386 (6)	−0·1583 (6)	1·065 (1)	0·042 (6)
O(4″)	0·9760 (5)	−0·3550 (5)	0·8742 (8)	0·045 (5)
O(7″)	0·8468 (5)	−0·4779 (5)	0·8669 (9)	0·054 (5)
O(10″)	0·8235 (5)	−0·4203 (6)	1·1873 (9)	0·057 (6)
O(13″)	0·8617 (5)	−0·2337 (5)	1·3028 (8)	0·049 (5)
C(1′)	0·7526 (7)	0·0120 (8)	0·827 (1)	0·037 (7)
C(2′)	0·8408 (7)	−0·0201 (7)	0·772 (1)	0·038 (7)
C(3′)	0·9048 (7)	−0·0751 (8)	0·846 (1)	0·038 (7)
C(4′)	0·8803 (8)	−0·0987 (8)	0·988 (1)	0·045 (8)
C(5′)	0·7895 (8)	−0·0653 (8)	1·041 (1)	0·048 (8)
C(6′)	0·7278 (8)	−0·0088 (8)	0·969 (1)	0·051 (8)

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refinement. The O(1) atom of one of the perchlorate ions is extremely anisotropic. The positions of the H atoms were calculated. Block-diagonal least-squares refinement on *F*, anisotropic for the non-H atoms and isotropic for the H atoms, converged to $R = 0\cdot078$, $wR = 0\cdot107$, $(\Delta/\sigma)_{\max} = 0\cdot70$. A weighting scheme $w = (5\cdot56 + F_{\rm obs} + 0\cdot0179F_{\rm obs}^2)^{-1}$ was used. An empirical absorption correction was applied, with corrections in the range 0·82–1·53 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between −0·3 and 0·9 e Å^{-3}. The highest value was found in the vicinity of the two atoms which were placed at the position of the unknown peaks discussed above. Scattering factors were taken from Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Na and Cl was corrected for. All calculations were performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), unless stated otherwise.*

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

Na—O(7)	2·382 (10)	C(11)—N(10)	1·50 (2)
Na—O(8)	2·73 (1)	N(10)—C(4a)	1·38 (1)
Na—N(1″)	2·71 (1)	N(10)—C(10a)	1·40 (1)
Na—O(4″)	2·348 (8)	C(4a)—C(9a)	1·41 (2)
Na—O(7″)	2·469 (8)	C(8a)—C(10a)	1·42 (2)
Na—O(10″)	2·49 (1)	C(2″)—C(3″)	1·51 (1)
Na—O(13″)	2·384 (8)	C(2″)—N(1″)	1·45 (1)
Cl(1)—O(1)	1·36 (2)	C(3″)—O(4″)	1·43 (2)
Cl(1)—O(2)	1·41 (1)	C(5″)—C(6″)	1·48 (2)
Cl(1)—O(3)	1·396 (9)	C(5″)—O(4″)	1·45 (1)
Cl(1)—O(4)	1·36 (2)	C(6″)—O(7″)	1·43 (2)
Cl(2)—O(5)	1·44 (1)	C(8″)—C(9″)	1·49 (2)
Cl(2)—O(6)	1·429 (10)	C(8″)—O(7″)	1·42 (2)
Cl(2)—O(7)	1·451 (9)	C(9″)—O(10″)	1·43 (1)
Cl(2)—O(8)	1·42 (1)	C(11″)—C(12″)	1·49 (2)
C(1)—C(2)	1·36 (2)	C(11″)—O(10″)	1·44 (1)
C(1)—C(9a)	1·43 (1)	C(12″)—O(13″)	1·46 (2)
C(2)—C(3)	1·39 (2)	C(14″)—C(15″)	1·49 (2)
C(3)—C(4)	1·37 (2)	C(14″)—O(13″)	1·44 (1)
C(4)—C(4a)	1·40 (1)	C(15″)—N(1″)	1·50 (1)
C(5)—C(6)	1·36 (2)	N(1″)—C(4′)	1·41 (1)
C(5)—C(10a)	1·40 (1)	C(1′)—C(2′)	1·38 (1)
C(6)—C(7)	1·41 (2)	C(1′)—C(6′)	1·41 (2)
C(7)—C(8)	1·33 (2)	C(2′)—C(3′)	1·39 (2)
C(8)—C(8a)	1·43 (1)	C(3′)—C(4′)	1·43 (2)
C(9)—C(8a)	1·40 (1)	C(4′)—C(5′)	1·41 (2)
C(9)—C(9a)	1·43 (1)	C(5′)—C(6′)	1·38 (2)
C(9)—C(1′)	1·46 (2)		
O(7)—Na—O(8)	53·1 (3)	C(4)—C(4a)—C(9a)	120·9 (9)
O(7)—Na—N(1″)	116·1 (3)	N(10)—C(4a)—C(9a)	118·6 (9)
O(7)—Na—O(4″)	148·4 (3)	C(8)—C(8a)—C(9)	121·5 (10)
O(7)—Na—O(7″)	97·8 (3)	C(8)—C(8a)—C(10a)	116·6 (9)
O(7)—Na—O(10″)	88·1 (3)	C(9)—C(8a)—C(10a)	121·9 (9)
O(7)—Na—O(13″)	94·9 (3)	C(1)—C(9a)—C(9)	120 (1)
O(8)—Na—N(1″)	96·9 (4)	C(1)—C(9a)—C(4a)	117·8 (9)
O(8)—Na—O(4″)	96·2 (3)	C(9)—C(9a)—C(4a)	121·6 (9)
O(8)—Na—O(7″)	85·8 (3)	C(5)—C(10a)—N(10)	119·8 (10)
O(8)—Na—O(10″)	128·5 (4)	C(5)—C(10a)—C(8a)	121·8 (9)
O(8)—Na—O(13″)	136·4 (3)	N(10)—C(10a)—C(8a)	118·2 (8)
N(1″)—Na—O(4″)	70·0 (3)	C(3″)—C(2″)—N(1″)	113·9 (9)
N(1″)—Na—O(7″)	139·4 (3)	C(2″)—C(3″)—O(4″)	110 (1)
N(1″)—Na—O(10″)	133·1 (3)	C(6″)—C(5″)—O(4″)	108 (1)
N(1″)—Na—O(13″)	69·4 (3)	C(5″)—C(6″)—O(7″)	108·7 (10)
O(4″)—Na—O(7″)	69·4 (3)	C(9″)—C(8″)—O(7″)	109·9 (10)
O(4″)—Na—O(10″)	110·4 (3)	C(8″)—C(9″)—O(10″)	106 (1)
O(4″)—Na—O(13″)	115·4 (3)	C(12″)—C(11″)—O(10″)	106 (1)
O(7″)—Na—O(10″)	65·3 (3)	C(11″)—C(12″)—O(13″)	108·3 (10)
O(7″)—Na—O(13″)	131·9 (3)	C(15″)—C(14″)—O(13″)	108·0 (9)
N(10″)—Na—O(13″)	69·1 (3)	C(14″)—C(15″)—N(1″)	113·8 (9)
O(1)—Cl(1)—O(2)	105 (1)	Na—N(1″)—C(2″)	103·6 (6)
O(1)—Cl(1)—O(3)	110·9 (8)	Na—N(1″)—C(15″)	104·2 (7)
O(1)—Cl(1)—O(4)	114 (1)	Na—N(1″)—C(4′)	102·2 (6)
O(2)—Cl(1)—O(3)	110·7 (8)	C(2″)—N(1″)—C(15″)	113·2 (8)
O(2)—Cl(1)—O(4)	103·0 (10)	C(2″)—N(1″)—C(4′)	118·7 (10)
O(3)—Cl(1)—O(4)	113·3 (9)	C(15″)—N(1″)—C(4′)	112·6 (8)
O(5)—Cl(2)—O(6)	110·5 (6)	Na—O(4″)—C(3″)	115·6 (6)
O(5)—Cl(2)—O(7)	109·7 (6)	Na—O(4″)—C(5″)	109·8 (7)
O(5)—Cl(2)—O(8)	110·9 (6)	C(3″)—O(4″)—C(5″)	112·7 (9)
O(6)—Cl(2)—O(7)	108·1 (5)	Na—O(7″)—C(6″)	113·0 (7)
O(6)—Cl(2)—O(8)	110·9 (7)	Na—O(7″)—C(8″)	117·3 (6)
O(7)—Cl(2)—O(8)	106·7 (6)	C(6″)—O(7″)—C(8″)	114·6 (9)
C(2)—C(1)—C(9a)	120 (1)	Na—O(10″)—C(9″)	106·3 (8)
C(1)—C(2)—C(3)	120 (1)	Na—O(10″)—C(11″)	104·5 (7)
C(2)—C(3)—C(4)	122·8 (10)	C(9″)—O(10″)—C(11″)	114·6 (9)
C(3)—C(4)—C(4a)	118 (1)	Na—O(13″)—C(12″)	115·0 (6)
C(6)—C(5)—C(10a)	118 (1)	Na—O(13″)—C(14″)	111·9 (6)
C(5)—C(6)—C(7)	122 (1)	C(12″)—O(13″)—C(14″)	110·8 (8)
C(6)—C(7)—C(8)	120 (1)	C(9)—C(1′)—C(2′)	123 (1)
C(7)—C(8)—C(8a)	122 (1)	C(9)—C(1′)—C(6′)	118·7 (9)
C(8a)—C(9)—C(9a)	117·1 (10)	C(2′)—C(1′)—C(6′)	118 (1)
C(8a)—C(9)—C(1′)	122·5 (9)	C(1′)—C(2′)—C(3′)	123 (1)
C(9a)—C(9)—C(1′)	120·4 (9)	C(2′)—C(3′)—C(4′)	119·5 (10)
C(11)—N(10)—C(4a)	118·2 (8)	N(1″)—C(4′)—C(3′)	123·3 (10)
C(11)—N(10)—C(10a)	120·0 (8)	N(1″)—C(4′)—C(5′)	120 (1)
C(4a)—N(10)—C(10a)	121·9 (9)	C(3′)—C(4′)—C(5′)	116 (1)
Na—O(7)—Cl(2)	107·3 (5)	C(4′)—C(5′)—C(6′)	124 (1)
Na—O(8)—Cl(2)	92·7 (5)	C(1′)—C(6′)—C(5′)	119 (1)
C(4)—C(4a)—N(10)	120·4 (10)		

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′)

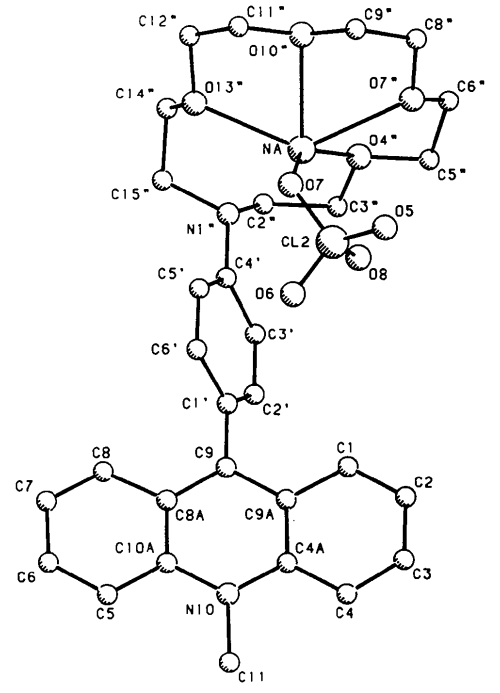

Fig. 1. Structure of $[C_{30}N_2O_4.Na.ClO_4]^+$ showing the numbering scheme.

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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 51852 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

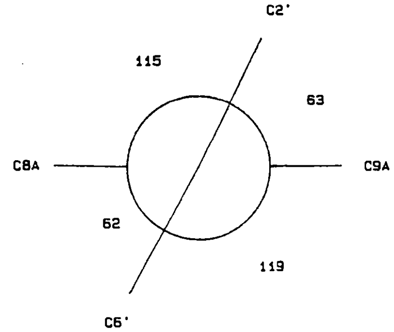

Fig. 2. The Newman projection along the C(9)—C(1') bond.

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. $C_{31}H_{37}N_2O_4^+.ClO_4^-$, $M_r = 601·1$, monoclinic, $P2_1/n$, $a = 22·332$ (5), $b = 13·813$ (3), $c = 9·650$ (3) Å, $\beta = 100·95$ (3)°, $V = 2923$ (2) Å^3, $Z = 4$, $D_x = 1·37$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·81$ cm^{-1}, $F(000) = 1272$, room temperature. Final $R = 0·069$ 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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