Here also one O atom of the perchlorate ion (O3) is markedly anisotropic.

For both structures: 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 *et al.*, 1976), unless stated otherwise.

Discussion. Final positional parameters for the non-H atoms for both structures are listed in Table 1.* Bond lengths and bond angles are listed in Table 2. A *PLUTO* (Motherwell & Clegg, 1978) drawing of molecule (*A*), showing the numbering scheme, is given in Fig. 1 [the numbering of (*B*) is similar] and the Newman projections along the C9—C1′ 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 of one of its constituent atoms from the plane is 0·082 Å. The phenyl ring of (*A*) is planar to within 0·011 Å. The angle between the two planes of (*A*) is 78°. For structure (*B*) the corresponding values are 0·124, 0·011 Å and 88° respectively. The angle between the two least-squares planes through the atoms C(1), C(2), C(3), C(4), C(4*a*), C(9*a*), C(9) and N(10) and the atoms C(5), C(6), C(7), C(8), C(8*a*), C(10*a*), C(9) and N(10) in (*B*) is 7°. The only significant difference between the two structures is in the twist angle. Matching of the two molecules [leaving out the perchlorates, all H atoms and C(7′) in structure (*B*)] resulted in an r.m.s. value of 0·11 Å. The largest distances between the corresponding atoms occur at C2′, C3′, C5′ and C6′ (about 0·2 Å).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52628 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystal Studies of Acridinium Dyes. XIV.* 10-Methyl-9-[2-methyl-4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium Potassium Dithiocyanate Acetonitrile Solvate

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Abstract. $C_{31}H_{37}N_2O_4^+.K^+.2SCN^-.CH_3CN$, $M_r = 698{\cdot}0$, triclinic, $P\bar{1}$, $a = 13{\cdot}460\ (2)$, $b = 15{\cdot}760\ (2)$, $c = 8{\cdot}646\ (1)$ Å, $\alpha = 101{\cdot}88\ (2)$, $\beta = 95{\cdot}23\ (2)$, $\gamma = 81{\cdot}52\ (2)°$, $V = 1771{\cdot}7\ (8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}31$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 27{\cdot}6$ cm^{-1}, $F(000) = 736$, room temperature. Final $R = 0{\cdot}048$ for 4101 observed reflections. The angle between the planes of the acridinium and the phenyl groups is 85°. The mean cavity radius of the crown ether is 1·47 Å. The K atom is six coordinated by the four O atoms of the crown ether and by two N atoms, one of a thiocyanate ion the other of the acetonitrile solvent.

Introduction. This is the fourteenth paper in a series of acridinium dyes. In this case the phenyl ring is

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* Part XIII, preceding paper.

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

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

	x	*y*	*z*	U_{eq}(Å^2)
K	0·71855 (5)	0·39274 (5)	0·59412 (8)	0·0490 (4)
S(1)	0·77070 (9)	0·79844 (8)	1·4890 (1)	0·0817 (7)
S(2)	0·6888 (1)	0·13484 (8)	0·1352 (1)	0·0827 (7)
C(1)	0·9206 (3)	−0·0389 (2)	0·8259 (4)	0·048 (2)
C(2)	0·9688 (3)	−0·1030 (2)	0·8993 (5)	0·059 (2)
C(3)	0·9125 (3)	−0·1543 (2)	0·9628 (5)	0·064 (2)
C(4)	0·8105 (3)	−0·1446 (2)	0·9460 (4)	0·057 (2)
C(5)	0·4971 (3)	0·0022 (2)	0·7438 (4)	0·055 (2)
C(6)	0·4483 (3)	0·0692 (3)	0·6784 (5)	0·062 (2)
C(7)	0·4992 (3)	0·1297 (2)	0·6314 (5)	0·059 (2)
C(8)	0·6013 (3)	0·1222 (2)	0·6513 (4)	0·050 (2)
C(9)	0·7624 (2)	0·0443 (2)	0·7399 (3)	0·038 (2)
C(11)	0·5982 (3)	−0·1361 (3)	0·8828 (6)	0·073 (3)
C(12)	0·7479 (3)	0·7568 (2)	1·2987 (5)	0·065 (2)
C(13)	0·6524 (3)	0·2081 (2)	0·2889 (4)	0·057 (2)
N(10)	0·6555 (2)	−0·0720 (2)	0·8394 (3)	0·044 (1)
N(12)	0·7308 (3)	0·7279 (2)	1·1758 (4)	0·075 (2)
N(13)	0·6259 (3)	0·2609 (2)	0·3960 (4)	0·076 (2)
C(2″)	1·0047 (3)	0·3709 (2)	0·7027 (5)	0·055 (2)
C(3″)	0·9603 (3)	0·4653 (2)	0·7356 (5)	0·061 (2)
C(5″)	0·8287 (4)	0·5609 (3)	0·8818 (6)	0·096 (3)
C(6″)	0·7730 (4)	0·6103 (3)	0·7716 (7)	0·093 (3)
C(8″)	0·6353 (7)	0·6184 (4)	0·5940 (9)	0·187 (6)
C(9″)	0·6028 (5)	0·5872 (4)	0·4622 (6)	0·131 (4)
C(11″)	0·7016 (3)	0·5029 (3)	0·2579 (5)	0·071 (3)
C(12″)	0·7587 (3)	0·4143 (3)	0·2102 (4)	0·065 (2)
C(14″)	0·8910 (3)	0·3158 (2)	0·2961 (4)	0·053 (2)
C(15″)	0·9776 (3)	0·3081 (2)	0·4191 (4)	0·053 (2)
N(1″)	0·9465 (2)	0·3158 (2)	0·5804 (3)	0·045 (1)
O(4″)	0·8690 (2)	0·4735 (2)	0·8118 (3)	0·064 (2)
O(7″)	0·6865 (3)	0·5704 (2)	0·7037 (4)	0·087 (2)
O(10″)	0·6438 (2)	0·5026 (2)	0·3865 (3)	0·074 (2)
O(13″)	0·8347 (2)	0·4005 (1)	0·3329 (3)	0·054 (1)
C(1′)	0·8180 (2)	0·1106 (2)	0·6964 (4)	0·039 (2)
C(2′)	0·8593 (2)	0·0983 (2)	0·5501 (4)	0·043 (2)
C(3′)	0·9039 (2)	0·1659 (2)	0·5151 (4)	0·044 (2)
C(4′)	0·9093 (2)	0·2452 (2)	0·6202 (4)	0·041 (2)
C(5′)	0·8686 (3)	0·2552 (2)	0·7675 (4)	0·046 (2)
C(6′)	0·8238 (3)	0·1889 (2)	0·8041 (4)	0·045 (2)
C(7′)	0·8536 (3)	0·0149 (2)	0·4294 (5)	0·064 (2)
C(4*a*)	0·7581 (2)	−0·0813 (2)	0·8640 (3)	0·043 (2)
C(8*a*)	0·6574 (2)	0·0533 (2)	0·7200 (4)	0·042 (2)
C(9*a*)	0·8133 (2)	−0·0245 (2)	0·8079 (4)	0·041 (2)
C(10*a*)	0·6038 (2)	−0·0070 (2)	0·7684 (4)	0·044 (2)
C(1*s*)	0·4943 (5)	0·3300 (5)	1·0142 (8)	0·134 (6)
C(2*s*)	0·5568 (3)	0·3631 (3)	0·9214 (5)	0·077 (3)
N(*s*)	0·6053 (4)	0·3892 (4)	0·8506 (5)	0·111 (4)

substituted with a methyl group and an aza-15-crown-5 group, which has formed a complex with potassium thiocyanate.

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

K—N(13)	2·778 (4)	C(2″)—N(1″)	1·469 (4)
K—O(4″)	2·889 (3)	C(3″)—O(4″)	1·423 (5)
K—O(7″)	2·748 (3)	C(5″)—C(6″)	1·442 (7)
K—O(10″)	2·769 (3)	C(5″)—O(4″)	1·433 (5)
K—O(13″)	2·893 (3)	C(6″)—O(7″)	1·426 (6)
K—N(*s*)	2·817 (5)	C(8″)—C(9″)	1·214 (9)
S(1)—C(12)	1·660 (4)	C(8″)—O(7″)	1·402 (8)
S(2)—C(13)	1·631 (4)	C(9″)—O(10″)	1·414 (6)
C(1)—C(2)	1·356 (5)	C(11″)—C(12″)	1·488 (5)
C(1)—C(9*a*)	1·428 (5)	C(11″)—O(10″)	1·415 (6)
C(2)—C(3)	1·403 (6)	C(12″)—O(13″)	1·432 (4)
C(3)—C(4)	1·357 (6)	C(14″)—C(15″)	1·514 (5)
C(4)—C(4*a*)	1·411 (5)	C(14″)—O(13″)	1·424 (4)
C(5)—C(6)	1·356 (5)	C(15″)—N(1″)	1·468 (5)
C(5)—C(10*a*)	1·424 (5)	N(1″)—C(4′)	1·401 (4)
C(6)—C(7)	1·396 (6)	C(1′)—C(2′)	1·393 (5)
C(7)—C(8)	1·359 (5)	C(1′)—C(6′)	1·392 (4)
C(8)—C(8*a*)	1·429 (5)	C(2′)—C(3′)	1·393 (5)
C(9)—C(1′)	1·496 (5)	C(2′)—C(7′)	1·508 (4)
C(9)—C(8*a*)	1·398 (4)	C(3′)—C(4′)	1·393 (4)
C(9)—C(9*a*)	1·400 (4)	C(4′)—C(5′)	1·401 (5)
C(11)—N(10)	1·482 (6)	C(5′)—C(6′)	1·383 (5)
C(12)—N(12)	1·085 (5)	C(4*a*)—C(9*a*)	1·426 (5)
C(13)—N(13)	1·154 (5)	C(8*a*)—C(10*a*)	1·421 (5)
N(10)—C(4*a*)	1·369 (4)	C(1*s*)—C(2*s*)	1·43 (1)
N(10)—C(10*a*)	1·370 (4)	C(2*s*)—N(*s*)	1·107 (8)
C(2″)—C(3″)	1·499 (5)		

N(13)—K—O(4″)	158·49 (9)	C(2″)—N(1″)—C(15″)	114·0 (3)
N(13)—K—O(7″)	140·1 (1)	C(2″)—N(1″)—C(4′)	118·5 (3)
N(13)—K—O(10″)	88·5 (1)	C(15″)—N(1″)—C(4′)	119·1 (2)
N(13)—K—O(13″)	88·4 (1)	K—O(4″)—C(3″)	110·0 (2)
N(13)—K—N(*s*)	92·6 (1)	K—O(4″)—C(5″)	109·7 (2)
O(4″)—K—O(7″)	61·44 (8)	C(3″)—O(4″)—C(5″)	115·6 (3)
O(4″)—K—O(10″)	108·84 (9)	K—O(7″)—C(6″)	116·0 (2)
O(4″)—K—O(13″)	89·36 (8)	K—O(7″)—C(8″)	114·6 (3)
O(4″)—K—N(*s*)	90·0 (1)	C(6″)—O(7″)—C(8″)	109·0 (5)
O(7″)—K—O(10″)	60·32 (9)	K—O(10″)—C(9″)	113·8 (3)
O(7″)—K—O(13″)	95·61 (9)	K—O(10″)—C(11″)	118·1 (2)
O(7″)—K—N(*s*)	83·1 (1)	C(9″)—O(10″)—C(11″)	113·4 (4)
O(10″)—K—O(13″)	60·26 (8)	K—O(13″)—C(12″)	102·9 (2)
O(10″)—K—N(*s*)	119·0 (1)	K—O(13″)—C(14″)	104·5 (2)
O(13″)—K—N(*s*)	178·7 (1)	C(12″)—O(13″)—C(14″)	111·1 (2)
C(2)—C(1)—C(9*a*)	121·0 (3)	C(9)—C(1′)—C(2′)	122·4 (3)
C(1)—C(2)—C(3)	119·6 (3)	C(9)—C(1′)—C(6′)	118·1 (3)
C(2)—C(3)—C(4)	121·8 (4)	C(2′)—C(1′)—C(6′)	119·5 (3)
C(3)—C(4)—C(4*a*)	120·1 (4)	C(1′)—C(2′)—C(3′)	118·6 (3)
C(6)—C(5)—C(10*a*)	119·7 (4)	C(1′)—C(2′)—C(7′)	121·2 (3)
C(5)—C(6)—C(7)	122·3 (3)	C(3′)—C(2′)—C(7′)	120·2 (3)
C(6)—C(7)—C(8)	119·6 (4)	C(2′)—C(3′)—C(4′)	122·8 (3)
C(7)—C(8)—C(8*a*)	121·1 (4)	N(1″)—C(4′)—C(3′)	122·9 (3)
C(1′)—C(9)—C(8*a*)	119·7 (3)	N(1″)—C(4′)—C(5′)	119·6 (3)
C(1′)—C(9)—C(9*a*)	121·1 (3)	C(3′)—C(4′)—C(5′)	117·3 (3)
C(8*a*)—C(9)—C(9*a*)	119·1 (3)	C(4′)—C(5′)—C(6′)	120·6 (3)
S(1)—C(12)—N(12)	177·6 (4)	C(1′)—C(6′)—C(5′)	121·1 (3)
S(2)—C(13)—N(13)	178·8 (4)	C(4)—C(4*a*)—N(10)	121·7 (3)
C(11)—N(10)—C(4*a*)	119·6 (3)	C(4)—C(4*a*)—C(9*a*)	119·1 (3)
C(11)—N(10)—C(10*a*)	118·5 (3)	N(10)—C(4*a*)—C(9*a*)	119·2 (3)
C(4*a*)—N(10)—C(10*a*)	121·9 (3)	C(8)—C(8*a*)—C(9)	121·7 (3)
K—N(13)—C(13)	132·7 (3)	C(8)—C(8*a*)—C(10*a*)	118·4 (3)
C(3″)—C(2″)—N(1″)	113·6 (3)	C(9)—C(8*a*)—C(10*a*)	119·9 (3)
C(2″)—C(3″)—O(4″)	109·0 (3)	C(1)—C(9*a*)—C(9)	121·7 (3)
C(6″)—C(5″)—O(4″)	114·5 (4)	C(1)—C(9*a*)—C(4*a*)	118·2 (3)
C(5″)—C(6″)—O(7″)	110·2 (4)	C(9)—C(9*a*)—C(4*a*)	120·1 (3)
C(9″)—C(8″)—O(7″)	125·3 (5)	C(5)—C(10*a*)—N(10)	121·3 (3)
C(8″)—C(9″)—O(10″)	120·0 (6)	C(5)—C(10*a*)—C(8*a*)	119·1 (3)
C(12″)—C(11″)—O(10″)	108·7 (4)	N(10)—C(10*a*)—C(8*a*)	119·6 (3)
C(11″)—C(12″)—O(13″)	108·2 (3)	C(1*s*)—C(2*s*)—N(*s*)	179·5 (5)
C(15″)—C(14″)—O(13″)	109·2 (3)	K—N(*s*)—C(2*s*)	157·7 (4)
C(14″)—C(15″)—N(1″)	114·2 (3)		

Experimental. A brown plate-shaped crystal (dimensions 0·08 × 0·20 × 0·30 mm approximately) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation and ω–2θ scans. A total of 5319 unique reflections was measured within the range $-15 \le h \le 15$, $-17 \le k \le 17$, $0 \le l \le 9$. Of these, 4101 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 (301, $0\bar{1}\bar{1}$) were measured hourly, no significant decrease was measured during the 60 h collection time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $60 < 2\theta < 72°$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods using *SIMPEL* (Schenk & Kiers, 1983). After isotropic refinement of the non-H atoms, a ΔF synthesis revealed three peaks, which were interpreted as acetonitrile, one of the solvents used during crystallization of the compound. The positions of the H atoms were calculated. During refinement atom C(8″) showed considerable apparent thermal anisotropy. The two H atoms bonded to this atom were not stable, so these H atoms were kept fixed at their calculated positions during refinement with $U = 0{\cdot}08$ Å^2.

Block-diagonal least-squares refinement on F, anisotropic for the non-H atoms and isotropic for the H atoms, converged to $R = 0{\cdot}048$, $wR = 0{\cdot}064$, $(\Delta/\sigma)_{\max} = 0{\cdot}96$. A weighting scheme $w = (8{\cdot}66 + F_o + 0{\cdot}007F_o^2)^{-1}$ was used. The isotropic secondary-extinction coefficient refined to $1{\cdot}2\,(7) \times 10^{-3}$ (Zachariasen, 1968). An empirical absorption correction was applied, with corrections in the range 0·85–1·20 (*DIFABS*; Walker & Stuart, 1983). A final difference synthesis revealed residual electron density between $-0{\cdot}3$ and $0{\cdot}3$ e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) and from *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for K and S was corrected for. All calculations were performed with *XRAY76* (Stewart *et al.*, 1976), unless stated otherwise.

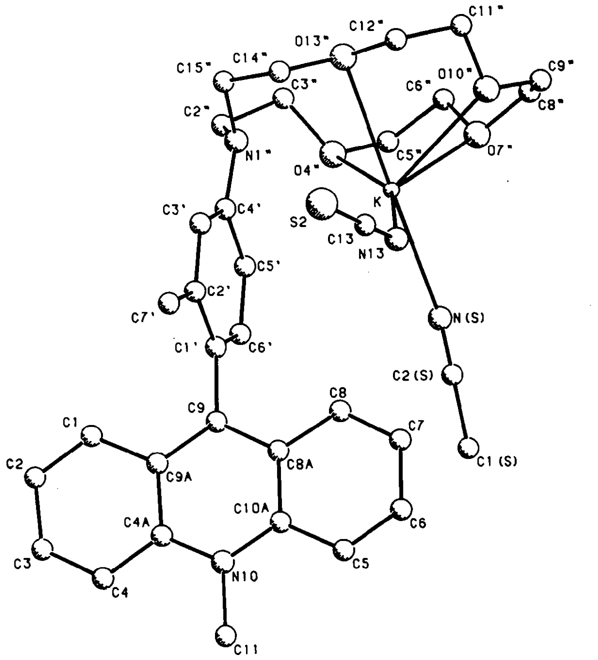

Fig. 1. Structure of $[C_{31}H_{37}N_2O_4.K.SCN.CH_3CN]^+$ showing the numbering scheme.

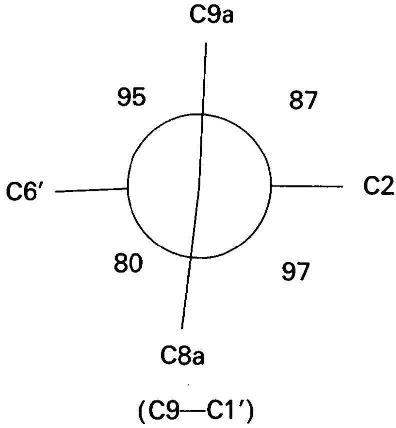

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

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 maximum distance of one of its constituent atoms from this plane is 0·089 Å. The phenyl ring is planar to within 0·005 Å. The angle between the two planes is 85°. The O atoms of the crown ether alternate about 0·13 Å above and below their mean plane; the N atom lies 0·96 Å below this plane. For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1·47 Å was obtained. The distance from the K ion to the centre of gravity of the hetero atoms in the crown ether is 1·58 Å, the angle N(1″)–centre of gravity–K is 88°. The K ion is coordinated by the four O atoms of the crown ether and by two N atoms, one of a thiocyanate ion, the other of the acetonitrile.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52629 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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