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

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Abstract. $C_{31}H_{37}N_2O_4^+.Na^+.ClO_4^-.SCN^-$, $M_r = 682{\cdot}2$, monoclinic, $P2_1/a$, $a = 14{\cdot}424\,(2)$, $b = 13{\cdot}736\,(3)$, $c = 18{\cdot}522\,(3)$ Å, $\beta = 112{\cdot}07\,(1)°$, $V = 3401\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 21{\cdot}3$ cm^{-1}, $F(000) = 1432$, room temperature. Final $R = 0{\cdot}097$ for 1508 observed reflections. The angle between acridinium and the phenyl group is 82°. The mean cavity radius of the crown ether is 1·08 Å. The Na atom is five coordinated by the four O atoms of the crown ether and by the N atom of the thiocyanate ion.

Introduction. This is the fifteenth paper in a series of acridinium dyes. In this case the phenyl ring is substituted with a methyl group and an aza-15-crown-5 group, which has formed a complex with sodium thiocyanate.

Experimental. An orange-red plate-shaped crystal (dimensions 0·10 × 0·18 × 0·25 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 3489 unique reflections was measured within the range $-14 \le h \le 13$, $0 \le k \le 13$, $0 \le l \le 18$. Of these, 1508 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·50 Å^{-1}. Two standard reflections ($\bar{3}12$, 003) were measured hourly, 13% decrease was measured during the 40 h collection time, which was corrected for. The gradual deterioration of the crystal is reflected in the relatively low number of observed reflections. 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 solved by direct methods using *SIMPEL* (Schenk & Kiers, 1983). The positions of the H atoms were calculated and kept fixed during refinement with $U = 0{\cdot}06$ Å^2. Block-diagonal least-squares refinement on F, anisotropic for the non-H atoms, converged to $R = 0{\cdot}097$, $wR = 0{\cdot}139$, $(\Delta/\sigma)_{\max} = 0{\cdot}83$. Three O atoms of the perchlorate ion [O(2), O(3) and O(4)] were extremely anisotropic. A weighting scheme $w = (5{\cdot}48 + F_o + 0{\cdot}015F_o^2)^{-1}$ was used. The isotropic secondary-extinction coefficient refined to 1·1 (4) × 10^{-3} (Zachariasen, 1968).

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

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

	x	y	z	$U_{\rm eq}$ (Å^2)
Na	0·4312 (4)	0·0102 (4)	0·7062 (3)	0·066 (4)
Cl	0·1172 (5)	0·0064 (5)	0·3899 (3)	0·140 (5)
S	0·7192 (4)	−0·1857 (4)	0·8538 (4)	0·103 (4)
C(1)	0·932 (1)	0·310 (1)	0·9332 (9)	0·07 (1)
C(2)	1·005 (1)	0·378 (1)	0·958 (1)	0·08 (1)
C(3)	1·069 (1)	0·385 (1)	1·035 (1)	0·10 (2)
C(4)	1·063 (1)	0·324 (1)	1·0893 (9)	0·07 (1)
C(5)	0·901 (1)	0·044 (1)	1·1578 (9)	0·08 (1)
C(6)	0·839 (1)	−0·029 (1)	1·1315 (8)	0·08 (1)
C(7)	0·777 (1)	−0·045 (1)	1·055 (1)	0·08 (1)
C(8)	0·778 (1)	0·018 (1)	0·9982 (9)	0·06 (1)
C(9)	0·8470 (9)	0·1678 (9)	0·9653 (7)	0·039 (8)
C(11)	1·044 (1)	0·197 (1)	1·2041 (9)	0·09 (1)
C(12)	0·628 (1)	−0·111 (1)	0·8297 (8)	0·06 (1)
N(10)	0·9780 (8)	0·1877 (9)	1·1215 (6)	0·059 (8)
N(12)	0·560 (1)	−0·059 (1)	0·8137 (8)	0·09 (1)
O(1)	0·044 (2)	−0·044 (2)	0·330 (1)	0·29 (3)
O(2)	0·052 (2)	0·076 (2)	0·411 (3)	0·42 (5)
O(3)	0·197 (2)	0·049 (2)	0·388 (2)	0·34 (3)
O(4)	0·163 (4)	−0·056 (3)	0·442 (2)	0·56 (5)
C(2″)	0·490 (1)	0·216 (1)	0·6241 (9)	0·07 (1)
C(3″)	0·381 (1)	0·192 (1)	0·592 (1)	0·09 (1)
C(5″)	0·247 (2)	0·152 (2)	0·631 (1)	0·13 (2)
C(6″)	0·215 (2)	0·095 (3)	0·670 (2)	0·22 (3)
C(8″)	0·217 (2)	−0·081 (2)	0·691 (2)	0·18 (3)
C(9″)	0·237 (2)	−0·142 (2)	0·642 (1)	0·14 (2)
C(11″)	0·363 (1)	−0·185 (1)	0·595 (1)	0·09 (1)
C(12″)	0·468 (1)	−0·163 (1)	0·6091 (9)	0·07 (1)
C(14″)	0·580 (1)	−0·034 (1)	0·6174 (8)	0·07 (1)
C(15″)	0·578 (1)	0·074 (1)	0·6010 (8)	0·08 (1)
N(1″)	0·5538 (9)	0·1306 (9)	0·6584 (7)	0·063 (8)
O(4″)	0·3531 (8)	0·1590 (8)	0·6516 (7)	0·092 (8)
O(7″)	0·2647 (9)	0·015 (1)	0·7121 (7)	0·11 (1)
O(10″)	0·3403 (7)	−0·1405 (8)	0·6569 (6)	0·079 (7)
O(13″)	0·4792 (7)	−0·0619 (7)	0·6044 (5)	0·067 (7)
C(1′)	0·774 (1)	0·163 (1)	0·8839 (8)	0·05 (1)
C(2′)	0·797 (1)	0·118 (1)	0·8271 (9)	0·07 (1)
C(3′)	0·723 (1)	0·108 (1)	0·7504 (8)	0·06 (1)
C(4′)	0·629 (1)	0·146 (1)	0·7343 (9)	0·06 (1)
C(5′)	0·607 (1)	0·193 (1)	0·7926 (8)	0·05 (1)
C(6′)	0·680 (1)	0·200 (1)	0·8681 (8)	0·053 (9)
C(7′)	0·899 (1)	0·073 (1)	0·845 (1)	0·09 (1)
C(4*a*)	0·987 (1)	0·250 (1)	1·0661 (8)	0·055 (9)
C(8*a*)	0·845 (1)	0·100 (1)	1·0200 (8)	0·056 (9)
C(9*a*)	0·922 (1)	0·242 (1)	0·9890 (8)	0·05 (1)
C(10*a*)	0·911 (1)	0·109 (1)	1·1007 (9)	0·07 (1)

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* Part XIV, preceding paper.

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

Na—N(12)	2·35 (1)	N(10)—C(10*a*)	1·40 (2)
Na—O(4″)	2·37 (1)	C(2″)—C(3″)	1·49 (2)
Na—O(7″)	2·44 (2)	C(2″)—N(1″)	1·48 (2)
Na—O(10″)	2·44 (1)	C(3″)—O(4″)	1·39 (3)
Na—O(13″)	2·45 (1)	C(5″)—C(6″)	1·28 (5)
Cl—O(1)	1·40 (2)	C(5″)—O(4″)	1·43 (3)
Cl—O(2)	1·49 (4)	C(6″)—O(7″)	1·38 (4)
Cl—O(3)	1·30 (3)	C(8″)—C(9″)	1·34 (5)
Cl—O(4)	1·28 (4)	C(8″)—O(7″)	1·46 (3)
S—C(12)	1·60 (2)	C(9″)—O(10″)	1·42 (3)
C(1)—C(2)	1·35 (2)	C(11″)—C(12″)	1·47 (3)
C(1)—C(9*a*)	1·44 (2)	C(11″)—O(10″)	1·44 (2)
C(2)—C(3)	1·39 (3)	C(12″)—O(13″)	1·41 (2)
C(3)—C(4)	1·35 (3)	C(14″)—C(15″)	1·51 (2)
C(4)—C(4*a*)	1·42 (2)	C(14″)—O(13″)	1·43 (2)
C(5)—C(6)	1·32 (2)	C(15″)—N(1″)	1·47 (2)
C(5)—C(10*a*)	1·43 (2)	N(1″)—C(4′)	1·43 (2)
C(6)—C(7)	1·37 (2)	C(1′)—C(2′)	1·36 (2)
C(7)—C(8)	1·37 (3)	C(1′)—C(6′)	1·37 (2)
C(8)—C(8*a*)	1·44 (2)	C(2′)—C(3′)	1·43 (2)
C(9)—C(1′)	1·48 (2)	C(2′)—C(7′)	1·52 (2)
C(9)—C(8*a*)	1·38 (2)	C(3′)—C(4′)	1·37 (2)
C(9)—C(9*a*)	1·43 (2)	C(4′)—C(5′)	1·39 (2)
C(11)—N(10)	1·47 (2)	C(5′)—C(6′)	1·40 (2)
C(12)—N(12)	1·16 (2)	C(4*a*)—C(9*a*)	1·39 (2)
N(10)—C(4*a*)	1·38 (2)	C(8*a*)—C(10*a*)	1·45 (2)

N(12)—Na—O(4″)	143·7 (5)	Na—O(7″)—C(8″)	110 (1)
N(12)—Na—O(7″)	116·6 (6)	C(6″)—O(7″)—C(8″)	118 (2)
N(12)—Na—O(10″)	96·8 (5)	Na—O(10″)—C(9″)	118 (1)
N(12)—Na—O(13″)	97·4 (5)	Na—O(10″)—C(11″)	114 (1)
O(4″)—Na—O(7″)	71·4 (5)	C(9″)—O(10″)—C(11″)	112 (1)
O(4″)—Na—O(10″)	118·0 (4)	Na—O(13″)—C(12″)	106 (1)
O(4″)—Na—O(13″)	104·3 (5)	Na—O(13″)—C(14″)	108·8 (8)
O(7″)—Na—O(10″)	68·8 (4)	C(12″)—O(13″)—C(14″)	113 (1)
O(7″)—Na—O(13″)	127·7 (4)	C(9)—C(1′)—C(2′)	122 (1)
O(10″)—Na—O(13″)	68·6 (4)	C(9)—C(1′)—C(6′)	118 (1)
O(1)—Cl—O(2)	99 (2)	C(2′)—C(1′)—C(6′)	121 (1)
O(1)—Cl—O(3)	128 (2)	C(1′)—C(2′)—C(3′)	120 (1)
O(1)—Cl—O(4)	107 (2)	C(1′)—C(2′)—C(7′)	121 (1)
O(2)—Cl—O(3)	112 (2)	C(3′)—C(2′)—C(7′)	119 (2)
O(2)—Cl—O(4)	115 (3)	C(2′)—C(3′)—C(4′)	119 (2)
O(3)—Cl—O(4)	96 (3)	N(1″)—C(4′)—C(3′)	119 (1)
C(2)—C(1)—C(9*a*)	119 (1)	N(1″)—C(4′)—C(5′)	121 (1)
C(1)—C(2)—C(3)	122 (2)	C(3′)—C(4′)—C(5′)	120 (1)
C(2)—C(3)—C(4)	121 (2)	C(4′)—C(5′)—C(6′)	120 (1)
C(3)—C(4)—C(4*a*)	119 (1)	C(1′)—C(6′)—C(5′)	120 (1)
C(6)—C(5)—C(10*a*)	117 (1)	C(4)—C(4*a*)—N(10)	119 (1)
C(5)—C(6)—C(7)	126 (2)	C(4)—C(4*a*)—C(9*a*)	121 (1)
C(6)—C(7)—C(8)	120 (2)	N(10)—C(4*a*)—C(9*a*)	120 (1)
C(7)—C(8)—C(8*a*)	119 (1)	C(8)—C(8*a*)—C(9)	121 (1)
C(1′)—C(9)—C(8*a*)	121 (1)	C(8)—C(8*a*)—C(10*a*)	118 (1)
C(1′)—C(9)—C(9*a*)	121 (1)	C(9)—C(8*a*]—C(10*a*)	121 (1)
C(8*a*)—C(9)—C(9*a*)	119 (1)	C(1)—C(9*a*)—C(9)	121 (1)
S—C(12)—N(12)	177 (2)	C)1)—C(9*a*)—C(4*a*)	118 (1)
C(11)—N(10)—C(4*a*)	121 (1)	C(9)—C(9*a*)—C(4*a*)	121 (1)
C(11)—N(10)—C(10*a*)	118 (1)	C(?5)—C(10*a*)—N(10)	122 (1)
C(4*a*)—N(10)—C(10*a*)	121 (1)	C(5)—C(10*a*)—C(8*a*)	120 (1)
Na—N(12)—C(12)	142 (1)	N(10)—C(10*a*)—C(9*a*)	118 (1)
C(3″)—C(2″)—N(1″)	113 (1)		
C(2″)—C(3″)—O(4″)	110 (1)		
C(6″)—C(5″)—O(4″)	118 (2)		
C(5″)—C(6″)—O(7″)	126 (3)		
C(9″)—C(8″)—O(7″)	123 (3)		
C(8″)—C(9″)—O(10″)	110 (2)		
C(12″)—C(11″)—O(10″)	108 (1)		
C(11″)—C(12″)—O(13″)	109 (1)		
C(15″)—C(14″)—O(13″)	107 (1)		
C(14″)—C(15″)—N(1″)	111 (1)		
C(2″)—N(1″)—C(15″)	113 (1)		
C(2″)—N(1″)—C(4′)	115 (1)		
C(15″)—N(1″)—C(4′)	119 (1)		
Na—O(4″)—C(3″)	113 (1)		
Na—O(4″)—C(5″)	110 (1)		
C(3″)—O(4″)—C(5″)	114 (1)		
Na—O(7″)—C(6″)	108 (2)		

An empirical absorption correction was applied, with corrections in the range 0·71–1·33 (*DIFABS*; Walker & Stuart, 1983). A final difference synthesis revealed residual electron density between −0·3 and 0·8 e Å^{-3}. Scattering factors were taken from Cromer & Mann (1968) and from *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Na, Cl and S was corrected for. All calculations were performed with *XRAY76* (Stewart *et al.*, 1976), unless stated otherwise.

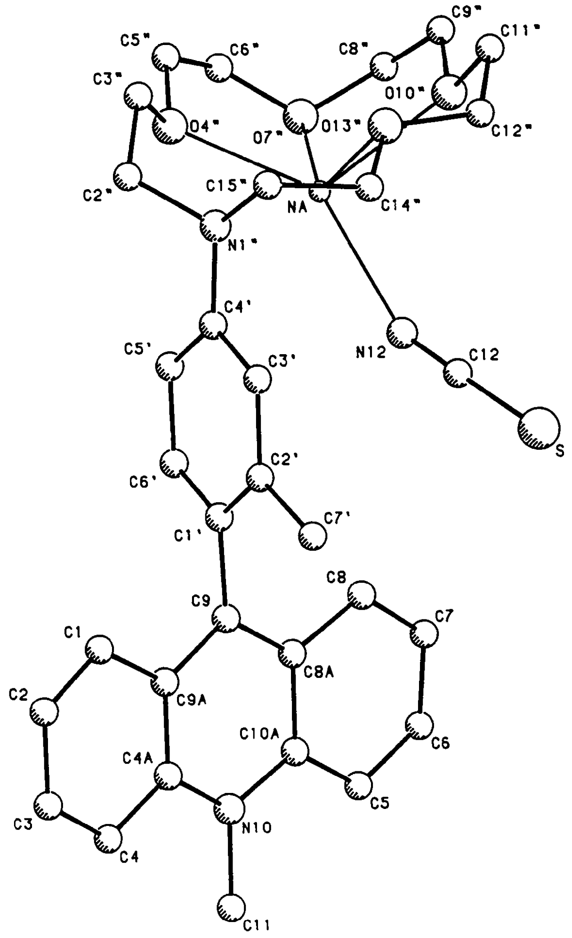

Fig. 1. Structure of $[C_{31}H_{37}N_2O_4.Na.SCN]^+$ showing the numbering scheme.

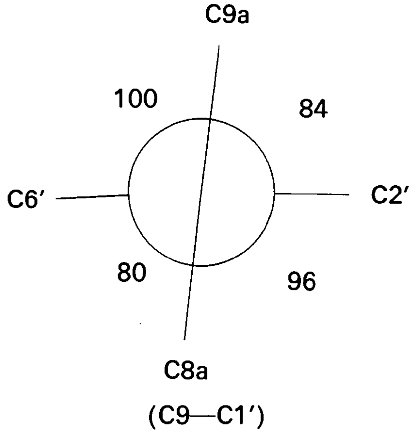

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

Discussion. Final positional parameters for the non-H atoms are listed in Table 1, and bond lengths and 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 0·103 Å. The phenyl ring is planar to within 0·007 Å. The angle between the two planes is 82°. The O atoms of the crown ether alternate about 0·10 Å above and below their mean plane; the N atom lies 1·24 Å below this plane. For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1·08 Å was obtained. The distance from the Na ion to the centre of gravity of the hetero atoms in the crown ether is 0·87 Å, the angle N(1″)–centre of gravity–Na is 87°. The Na ion is coordinated by the four O atoms of the crown ether and by the N atom of the thiocyanate ion.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths 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 52630 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

International Tables for X-ray Crystallography (1974). Vol. IV, p.55. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Mathieu, F., Metz, B., Moras, B & Weiss, R. (1978). *J. Am. Chem. Soc.* **100**, 4412–4416.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Schenk, H. & Kiers, C. T. (1983). *SIMPEL83, a Program System for Direct Methods.* In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 200–205. Oxford: Clarendon Press.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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Crystal Studies of Acridinium Dyes. XVI.* Another Modification of 10-Methyl-9-[4-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)phenyl]acridinium Silver Diperchlorate Acetonitrile Solvate

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Abstract. $C_{30}H_{35}N_2O_4^+.Ag^+.2ClO_4^-.CH_3CN$, M_r = 835·5, monoclinic, $P2_1/a$, a = 11·805 (5), b = 26·770 (18), c = 11·475 (5) Å, β = 100·37 (4)°, V = 3567 (4) Å^3, Z = 4, D_x = 1·56 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 7·7 cm^{-1}, F(000) = 1712, room temperature. Final R = 0·074 for 2873 observed reflections. The angle between the planes of the acridinium and the phenyl groups is 61°. The mean cavity radius of the crown ether is 1·15 Å. The Ag atom is coordinated by the five hetero atoms of the crown ether and the N atom of the acetonitrile solvent.

Introduction. This is the sixteenth paper in a series of acridinium dyes. In this case the phenyl ring is substituted with an aza-15-crown-5 group, which has formed a complex with silver perchlorate. This is the same compound as in the seventh paper of this series (Kronenberg, Reiss, Goubitz & Heijdenrijk, 1989) but the crystals contain a different solvent molecule, acetonitrile instead of dichloromethane.

Experimental. A red plate-shaped crystal (dimensions 0·15 × 0·30 × 0·40 mm approximately) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation and ω–2θ scans. A total of 6269 unique reflections was measured within the range $-13 \le h \le 13$, $0 \le k \le 30$, $0 \le l \le 13$. Of these, 2873 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·59 Å^{-1}. Three standard

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* Part XV, preceding paper.

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