

value of 1.28 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), while the N(1)—C(1) and N(1)—C(3) formal single bonds are shortened from the theoretical N—C(*sp*<sup>2</sup>) single-bond value of *ca* 1.45 Å, indicative of electron delocalization in the triazolo ring. The triazolo ring is planar to within ±0.004 Å in both structures. The angles C(11)—N(1)—C(3) and N(1)—C(3)—C(4) are 129.4 (10) and 123.7 (10)°, respectively, in (I), and 129.0 (2) and 124.1 (2)° in (II), so that the geometry of the N(1)—C(3) bond resembles that of a double bond, as in (III) and in the classical benzodiazepin-2-ones (Hamor & Martin, 1983).

The bond lengths at the C(6) carbonyl group appear to show that there is little if any conjugation between the O atom and the aromatic rings. The C—C bonds are in the range 1.479–1.516 Å and the C=O bonds are 1.205 (11) and 1.211 (3) Å, corresponding, respectively, to C(*sp*<sup>2</sup>)—C(*sp*<sup>2</sup>) single and C=O double bonds. These values are similar to those in 2-*tert*-butylbenzophenone (Wagner, Giri, Scaiano, Ward, Gabe & Lee, 1985) and other benzophenones in which the carbonyl O atom is not involved in hydrogen bonding (Faerman, Nyburg, Punte, Rivero, Vitale & Nudelman, 1985). The angle between the two aromatic rings is 73 (2)° in (I) and 61.1 (5)° in (II). The comparable dihedral angle in the alprazolam analogue (III) is similar, 63.5°.

In both structures intermolecular contacts involve only normal van der Waals interactions.

We thank Dr M. Gall and Dr D. J. Duchamp, Upjohn Company, for materials and structural parameters, Dr I. L. Martin for affinity measurements and the SERC for financial support (to HJK).

#### References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- FAERMAN, C., NYBURG, S. C., PUNTE, G., RIVERO, B. E., VITALE, A. A. & NUDELMAN, N. S. (1985). *Can. J. Chem.* **63**, 3374–3377.
- GALL, M., HESTER, J. B., RUDZIK, D. A. & LAHTI, R. A. (1976). *J. Med. Chem.* **19**, 1057–1064.
- HAMOR, T. A. & MARTIN, I. L. (1983). In *Progress in Medicinal Chemistry*, Vol. 20, edited by G. P. ELLIS & G. B. WEST, pp. 157–223. Amsterdam: Elsevier.
- HIRAI, K., FUJISHITA, T., ISHIBA, T., SUGIMOTO, H., MATSUTANI, S., TSUKINOKI, Y. & HIROSE, K. (1982). *J. Med. Chem.* **25**, 1466–1473.
- HIRAI, K., ISHIBA, H., SUGIMOTO, H., FUJISHITA, T., TSUKINOKI, Y. & HIROSE, K. (1981). *J. Med. Chem.* **24**, 20–27.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- KEMMISH, H. J. & HAMOR, T. A. (1988). *Acta Cryst.* **C44**, 1823–1825.
- LAHTI, R. A. & GALL, M. (1976). *J. Med. Chem.* **19**, 1064–1067.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1978). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WAGNER, P. J., GIRI, B. P., SCAIANO, J. C., WARD, D. L., GABE, E. & LEE, F. L. (1985). *J. Am. Chem. Soc.* **107**, 5483–5490.

*Acta Cryst.* (1990). **C46**, 462–465

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

BY LUDGER P. HÄMING, CELESTE A. REISS, KEES GOUBITZ AND DICK HEIJDENRIJK

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

(Received 13 March 1989; accepted 15 June 1989)

**Abstract.** C<sub>31</sub>H<sub>37</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>.Ba<sup>2+</sup>.3ClO<sub>4</sub><sup>-</sup>.C<sub>2</sub>H<sub>3</sub>N, *M*<sub>r</sub> = 978.4, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 22.089 (5), *b* = 13.707 (3), *c* = 13.081 (4) Å, β = 93.50 (2)°, *V* = 3953 (2) Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.64 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 12.8 cm<sup>-1</sup>, *F*(000) = 1976, room temperature. Final *R* = 0.056 for 4074 observed reflections. The angle between the acridinium and phenyl groups is 79°. The mean cavity radius for the crown ether is 1.51 Å. There are nine Ba—O distances in the range 2.77 (1)–3.00 (1) Å. In addition, there are

two larger Ba—O (perchlorate) and Ba—N distances of 3.29 (2) and 3.26 (1) Å respectively.

**Introduction.** The title compound is the tenth structure in a series of acridinium dyes (I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeven, 1989; II, IV: Reiss, Goubitz & Heijdenrijk, 1989*a,b*; III, VII: Kronenburg, Goubitz, Reiss & Heijdenrijk, 1989*a,b*; V, VIII: Goubitz, Reiss & Heijdenrijk, 1989*a,b*; VI: Zoutberg, Reiss, Goubitz & Heijdenrijk, 1989; IX: Reiss, Gou-

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

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1)	-0.0015 (1)	0.2034 (2)	0.1480 (2)	0.044 (1)
C(2)	0.2027 (2)	0.4251 (2)	0.3019 (3)	0.071 (2)
C(3)	0.1271 (1)	0.4089 (2)	-0.0553 (2)	0.048 (1)
C(1)	0.0360 (6)	0.1336 (9)	0.688 (1)	0.058 (7)
C(2)	0.0089 (8)	0.081 (1)	0.760 (1)	0.08 (1)
C(3)	-0.0240 (7)	0.131 (1)	0.832 (1)	0.075 (9)
C(4)	-0.0284 (6)	0.230 (1)	0.8342 (9)	0.070 (8)
C(5)	0.0191 (6)	0.5423 (10)	0.686 (1)	0.073 (9)
C(6)	0.0471 (6)	0.5939 (9)	0.613 (1)	0.068 (8)
C(7)	0.0813 (6)	0.5502 (9)	0.536 (1)	0.066 (8)
C(8)	0.0862 (6)	0.4489 (8)	0.5363 (9)	0.054 (7)
C(9)	0.0621 (5)	0.2891 (7)	0.6108 (7)	0.041 (5)
C(11)	-0.0399 (7)	0.435 (1)	0.834 (1)	0.09 (1)
N(10)	-0.0035 (4)	0.3844 (7)	0.7566 (7)	0.054 (6)
O(1)	-0.0438 (5)	0.225 (1)	0.0699 (7)	0.120 (10)
O(2)	-0.0304 (4)	0.1791 (8)	0.2372 (7)	0.077 (6)
O(3)	0.0406 (4)	0.1283 (6)	0.1215 (8)	0.073 (6)
O(4)	0.0376 (5)	0.2842 (8)	0.172 (1)	0.102 (8)
O(5)	0.1526 (7)	0.3635 (10)	0.2841 (10)	0.13 (1)
O(6)	0.1878 (6)	0.5216 (7)	0.276 (1)	0.12 (1)
O(7)	0.2457 (7)	0.390 (1)	0.2355 (10)	0.14 (1)
O(8)	0.2245 (6)	0.4176 (9)	0.4057 (8)	0.110 (9)
O(9)	0.1752 (5)	0.4067 (7)	0.0211 (9)	0.090 (7)
O(10)	0.1503 (6)	0.4181 (9)	-0.1534 (8)	0.098 (8)
O(11)	0.0881 (5)	0.4882 (7)	-0.0405 (8)	0.085 (7)
O(12)	0.0960 (4)	0.3175 (7)	-0.0491 (9)	0.083 (7)
C(4a)	-0.0009 (5)	0.2841 (9)	0.7569 (8)	0.049 (6)
C(8a)	0.0575 (5)	0.3923 (8)	0.6116 (7)	0.041 (6)
C(9a)	0.0331 (5)	0.2376 (8)	0.6834 (8)	0.043 (6)
C(10a)	0.0221 (5)	0.4398 (9)	0.6838 (8)	0.050 (6)
C(1s)	0.380 (1)	0.414 (2)	0.416 (2)	0.13 (2)
C(2s)	0.3837 (10)	0.334 (2)	0.491 (2)	0.13 (2)
N(1s)	0.375 (1)	0.274 (2)	0.542 (2)	0.19 (2)
Ba(2+)	0.16213 (3)	0.21703 (4)	0.12460 (5)	0.0386 (3)
C(2'')	0.2638 (5)	0.0736 (8)	0.3393 (8)	0.047 (6)
C(3'')	0.2929 (5)	0.1641 (10)	0.3033 (9)	0.056 (7)
C(5'')	0.3291 (6)	0.200 (1)	0.1380 (10)	0.065 (8)
C(6'')	0.3153 (5)	0.1750 (9)	0.027 (1)	0.058 (7)
C(8'')	0.2421 (7)	0.205 (1)	-0.110 (1)	0.074 (9)
C(9'')	0.2097 (7)	0.112 (1)	-0.1250 (10)	0.074 (9)
C(11'')	0.1290 (7)	0.018 (1)	-0.059 (1)	0.071 (9)
C(12'')	0.1611 (6)	0.0459 (9)	0.021 (1)	0.062 (8)
C(14'')	0.1854 (5)	-0.0596 (8)	0.197 (1)	0.057 (7)
C(15'')	0.1713 (6)	-0.0206 (7)	0.3003 (8)	0.048 (6)
N(1'')	0.1966 (4)	0.0775 (6)	0.3214 (6)	0.042 (5)
O(4'')	0.2795 (3)	0.1675 (6)	0.1916 (6)	0.057 (5)
O(7'')	0.2598 (4)	0.2227 (6)	-0.0061 (6)	0.058 (5)
O(10'')	0.1577 (4)	0.1113 (6)	-0.0602 (7)	0.068 (6)
O(13'')	0.1583 (3)	0.0021 (5)	0.1188 (5)	0.048 (4)
C(1')	0.0985 (5)	0.2390 (7)	0.5348 (7)	0.037 (5)
C(2')	0.1611 (5)	0.2338 (7)	0.5478 (7)	0.038 (5)
C(3')	0.1942 (5)	0.1805 (8)	0.4776 (8)	0.041 (5)
C(4')	0.1646 (4)	0.1309 (7)	0.3948 (6)	0.034 (5)
C(5')	0.1014 (5)	0.1400 (7)	0.3809 (7)	0.037 (5)
C(6')	0.0696 (5)	0.1920 (7)	0.4520 (8)	0.041 (5)
C(7')	0.1966 (5)	0.2850 (10)	0.6332 (8)	0.059 (7)

bitz, Zoutberg & Heijdenrijk, 1989). 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 barium perchlorate.

**Experimental.** A brown-yellow plate-shaped crystal (dimensions 0.08 × 0.45 × 0.45 mm approximately) was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and  $\omega$ - $2\theta$  scans. A total of 6904 unique reflections was measured within the range  $-26 \leq h \leq 26$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 15$ . Of these, 4074 were above the significance level of  $2.5\sigma(I)$ . The maximum value of  $(\sin\theta)/\lambda$  was  $0.59 \text{ Å}^{-1}$ . Two standard reflections (032, 600) were measured

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

C(1)—O(1)	1.37 (1)	O(12)—Ba(2 <sup>+</sup> )	2.96 (1)
C(1)—O(2)	1.404 (10)	C(4a)—C(9a)	1.41 (2)
C(1)—O(3)	1.444 (10)	C(8a)—C(10a)	1.42 (2)
C(1)—O(4)	1.43 (1)	C(1s)—C(2s)	1.47 (3)
C(2)—O(5)	1.40 (2)	C(2s)—N(1s)	1.08 (3)
C(2)—O(6)	1.40 (1)	Ba(2 <sup>+</sup> )—N(1'')	3.260 (8)
C(2)—O(7)	1.41 (2)	Ba(2 <sup>+</sup> )—O(4'')	2.770 (7)
C(2)—O(8)	1.42 (1)	Ba(2 <sup>+</sup> )—O(7'')	2.834 (8)
C(3)—O(9)	1.41 (1)	Ba(2 <sup>+</sup> )—O(10'')	2.815 (9)
C(3)—O(10)	1.42 (1)	Ba(2 <sup>+</sup> )—O(13'')	2.948 (7)
C(3)—O(11)	1.41 (1)	C(2'')—C(3'')	1.49 (2)
C(3)—O(12)	1.433 (10)	C(2'')—N(1'')	1.49 (1)
C(1)—C(2)	1.35 (2)	C(3'')—O(4'')	1.47 (1)
C(1)—C(9a)	1.43 (2)	C(5'')—C(6'')	1.50 (2)
C(2)—C(3)	1.40 (2)	C(5'')—O(4'')	1.41 (2)
C(3)—C(4)	1.36 (2)	C(6'')—O(7'')	1.43 (1)
C(4)—C(4a)	1.42 (2)	C(8'')—C(9'')	1.47 (2)
C(5)—C(6)	1.37 (2)	C(8'')—O(7'')	1.41 (2)
C(5)—C(10a)	1.41 (2)	C(9'')—O(10'')	1.47 (2)
C(6)—C(7)	1.43 (2)	C(11'')—C(12'')	1.51 (2)
C(7)—C(8)	1.39 (2)	C(11'')—O(10'')	1.43 (2)
C(8)—C(8a)	1.43 (2)	C(12'')—O(13'')	1.44 (2)
C(9)—C(8a)	1.42 (1)	C(14'')—C(15'')	1.50 (2)
C(9)—C(9a)	1.37 (1)	C(14'')—O(13'')	1.43 (1)
C(9)—C(1')	1.48 (1)	C(15'')—N(1'')	1.48 (1)
C(11)—N(10)	1.50 (2)	N(1'')—C(4')	1.43 (1)
N(10)—C(4a)	1.38 (2)	C(1')—C(2')	1.38 (1)
N(10)—C(10a)	1.37 (1)	C(1')—C(6')	1.38 (1)
O(3)—Ba(2 <sup>+</sup> )	2.945 (9)	C(2')—C(3')	1.41 (1)
O(4)—Ba(2 <sup>+</sup> )	3.00 (1)	C(2')—C(7')	1.50 (1)
O(5)—Ba(2 <sup>+</sup> )	2.91 (1)	C(3')—C(4')	1.41 (1)
O(7)—Ba(2 <sup>+</sup> )	3.29 (2)	C(4')—C(5')	1.40 (1)
O(9)—Ba(2 <sup>+</sup> )	2.95 (1)	C(5')—C(6')	1.40 (1)
C(12'')—C(11'')—O(10'')	110 (1)	Ba(2 <sup>+</sup> )—O(10'')—C(11'')	116.3 (7)
C(11'')—C(12'')—O(13'')	107.9 (10)	C(9'')—O(10'')—C(11'')	112.1 (10)
C(15'')—C(14'')—O(13'')	109.4 (9)	Ba(2 <sup>+</sup> )—O(13'')—C(12'')	118.4 (6)
C(14'')—C(15'')—N(1'')	113.3 (9)	Ba(2 <sup>+</sup> )—O(13'')—C(14'')	124.2 (6)
Ba(2 <sup>+</sup> )—N(1'')—C(2'')	109.1 (6)	C(12'')—O(13'')—C(14'')	109.0 (8)
Ba(2 <sup>+</sup> )—N(1'')—C(15'')	108.6 (6)	C(9')—C(1')—C(2')	121.3 (8)
Ba(2 <sup>+</sup> )—N(1'')—C(4')	97.4 (5)	C(9')—C(1')—C(6')	119.8 (9)
C(2'')—N(1'')—C(15'')	111.0 (8)	C(2')—C(1')—C(6')	118.8 (9)
C(2'')—N(1'')—C(4')	116.2 (8)	C(1')—C(2')—C(3')	120.0 (9)
C(15'')—N(1'')—C(4')	113.3 (8)	C(1')—C(2')—C(7')	122.7 (9)
Ba(2 <sup>+</sup> )—O(4'')—C(3'')	116.7 (6)	C(3')—C(2')—C(7')	117.3 (9)
Ba(2 <sup>+</sup> )—O(4'')—C(5'')	120.4 (7)	C(2')—C(3')—C(4')	121.1 (9)
C(3'')—O(4'')—C(5'')	112.8 (8)	N(1'')—C(4')—C(3')	122.7 (9)
Ba(2 <sup>+</sup> )—O(7'')—C(6'')	118.3 (7)	N(1'')—C(4')—C(5')	119.2 (8)
Ba(2 <sup>+</sup> )—O(7'')—C(8'')	113.6 (8)	C(3')—C(4')—C(5')	118.0 (9)
C(6'')—O(7'')—C(8'')	113.2 (10)	C(4')—C(5')—C(6')	119.8 (9)
Ba(2 <sup>+</sup> )—O(10'')—C(9'')	120.3 (7)	C(1')—C(6')—C(5')	122.2 (9)
O(1)—C(1)—O(2)	110.2 (6)	O(3)—Ba(2 <sup>+</sup> )—N(1'')	86.4 (2)
O(1)—C(1)—O(3)	113.2 (7)	O(3)—Ba(2 <sup>+</sup> )—O(13'')	137.5 (3)
O(1)—C(1)—O(4)	111.8 (8)	O(3)—Ba(2 <sup>+</sup> )—O(7'')	136.9 (3)
O(2)—C(1)—O(3)	111.3 (6)	O(3)—Ba(2 <sup>+</sup> )—O(10'')	78.0 (3)
O(2)—C(1)—O(4)	107.5 (7)	O(3)—Ba(2 <sup>+</sup> )—O(13'')	64.0 (2)
O(3)—C(1)—O(4)	102.5 (6)	O(4)—Ba(2 <sup>+</sup> )—O(5)	62.2 (4)
O(5)—C(2)—O(6)	111.0 (8)	O(4)—Ba(2 <sup>+</sup> )—O(7)	100.6 (3)
O(5)—C(2)—O(7)	104.3 (9)	O(4)—Ba(2 <sup>+</sup> )—O(9)	86.6 (3)
O(5)—C(2)—O(8)	109.6 (8)	O(4)—Ba(2 <sup>+</sup> )—O(12)	66.5 (3)
O(6)—C(2)—O(7)	109.3 (9)	O(4)—Ba(2 <sup>+</sup> )—N(1'')	100.9 (3)
O(6)—C(2)—O(8)	111.2 (9)	O(4)—Ba(2 <sup>+</sup> )—O(4'')	149.5 (3)
O(7)—C(2)—O(8)	111.3 (8)	O(4)—Ba(2 <sup>+</sup> )—O(7'')	149.0 (3)
O(9)—C(3)—O(10)	110.2 (7)	O(4)—Ba(2 <sup>+</sup> )—O(10'')	110.6 (3)
O(9)—C(3)—O(11)	111.0 (6)	O(4)—Ba(2 <sup>+</sup> )—O(13'')	106.7 (3)
O(9)—C(3)—O(12)	106.5 (6)	O(5)—Ba(2 <sup>+</sup> )—O(7)	41.4 (4)
O(10)—C(3)—O(11)	108.3 (7)	O(5)—Ba(2 <sup>+</sup> )—O(9)	74.6 (3)
O(10)—C(3)—O(12)	109.3 (7)	O(5)—Ba(2 <sup>+</sup> )—O(12)	100.1 (3)
O(11)—C(3)—O(12)	111.6 (6)	O(5)—Ba(2 <sup>+</sup> )—N(1'')	82.1 (3)
C(2)—C(1)—C(9a)	123 (1)	O(5)—Ba(2 <sup>+</sup> )—O(4'')	92.8 (4)
C(1)—C(2)—C(3)	118 (1)	O(5)—Ba(2 <sup>+</sup> )—O(7'')	120.3 (4)
C(2)—C(3)—C(4)	123 (1)	O(5)—Ba(2 <sup>+</sup> )—O(10'')	165.9 (3)
C(3)—C(4)—C(4a)	118 (1)	O(5)—Ba(2 <sup>+</sup> )—O(13'')	134.8 (3)
C(6)—C(5)—C(10a)	119 (1)	O(7)—Ba(2 <sup>+</sup> )—O(9)	60.0 (3)
C(5)—C(6)—C(7)	124 (1)	O(7)—Ba(2 <sup>+</sup> )—O(12)	103.9 (3)
C(6)—C(7)—C(8)	117 (1)	O(7)—Ba(2 <sup>+</sup> )—N(1'')	88.7 (3)
C(7)—C(8)—C(8a)	120 (1)	O(7)—Ba(2 <sup>+</sup> )—O(4'')	63.1 (3)
C(8a)—C(9)—C(9a)	118.1 (9)	O(7)—Ba(2 <sup>+</sup> )—O(7'')	79.6 (3)
C(8a)—C(9)—C(1')	120.5 (9)	O(7)—Ba(2 <sup>+</sup> )—O(10'')	137.3 (3)
C(9a)—C(9)—C(1')	121.3 (9)	O(7)—Ba(2 <sup>+</sup> )—O(13'')	138.3 (3)
C(11)—N(10)—C(4a)	119 (1)	O(9)—Ba(2 <sup>+</sup> )—O(12)	45.3 (3)
C(11)—N(10)—C(10a)	118 (1)	O(9)—Ba(2 <sup>+</sup> )—N(1'')	148.6 (3)
C(4a)—N(10)—C(10a)	122.5 (10)	O(9)—Ba(2 <sup>+</sup> )—O(4'')	104.2 (3)
C(1)—O(3)—Ba(2 <sup>+</sup> )	107.6 (5)	O(9)—Ba(2 <sup>+</sup> )—O(7'')	66.4 (3)
C(1)—O(4)—Ba(2 <sup>+</sup> )	105.5 (6)	O(9)—Ba(2 <sup>+</sup> )—O(10'')	93.4 (3)
C(2)—O(5)—Ba(2 <sup>+</sup> )	116.4 (8)	O(9)—Ba(2 <sup>+</sup> )—O(13'')	150.6 (3)
C(2)—O(7)—Ba(2 <sup>+</sup> )	97.9 (7)	O(12)—Ba(2 <sup>+</sup> )—N(1'')	163.4 (2)

Table 2 (cont.)

C(3)—O(9)—Ba(2 <sup>+</sup> )	104.6 (5)	O(12)—Ba(2 <sup>+</sup> )—O(4 <sup>''</sup> )	139.8 (3)
C(3)—O(12)—Ba(2 <sup>+</sup> )	103.5 (5)	O(12)—Ba(2 <sup>+</sup> )—O(7 <sup>''</sup> )	83.3 (3)
C(4)—C(4a)—N(10)	120 (1)	O(12)—Ba(2 <sup>+</sup> )—O(10 <sup>''</sup> )	65.9 (3)
C(4)—C(4a)—C(9a)	121 (1)	O(12)—Ba(2 <sup>+</sup> )—O(13 <sup>''</sup> )	115.6 (2)
N(10)—C(4a)—C(9a)	118.3 (10)	N(1 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(4 <sup>''</sup> )	55.8 (2)
C(8)—C(8a)—C(9)	120.0 (9)	N(1 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(7 <sup>''</sup> )	110.0 (2)
C(8)—C(8a)—C(10a)	119.6 (10)	N(1 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(10 <sup>''</sup> )	111.7 (2)
C(9)—C(8a)—C(10a)	120.3 (9)	N(1 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(13 <sup>''</sup> )	55.9 (2)
C(1)—C(9a)—C(9)	121 (1)	O(4 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(7 <sup>''</sup> )	57.7 (2)
C(1)—C(9a)—C(4a)	117 (1)	O(4 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(10 <sup>''</sup> )	97.4 (3)
C(9)—C(9a)—C(4a)	122.0 (10)	O(4 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(13 <sup>''</sup> )	77.8 (2)
C(5)—C(10a)—N(10)	121 (1)	O(7 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(10 <sup>''</sup> )	58.9 (2)
C(5)—C(10a)—C(8a)	120 (1)	O(7 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(13 <sup>''</sup> )	91.9 (2)
N(10)—C(10a)—C(8a)	118 (1)	O(10 <sup>''</sup> )—Ba(2 <sup>+</sup> )—O(13 <sup>''</sup> )	57.6 (2)
C(1s)—C(2s)—N(1s)	166 (3)	C(3 <sup>''</sup> )—C(2 <sup>''</sup> )—N(1 <sup>''</sup> )	111.5 (9)
O(3)—Ba(2 <sup>+</sup> )—O(4)	44.2 (3)	C(2 <sup>''</sup> )—C(3 <sup>''</sup> )—O(4 <sup>''</sup> )	106.0 (9)
O(3)—Ba(2 <sup>+</sup> )—O(5)	100.9 (4)	C(6 <sup>''</sup> )—C(5 <sup>''</sup> )—O(4 <sup>''</sup> )	106.9 (10)
O(3)—Ba(2 <sup>+</sup> )—O(7)	142.3 (3)	C(5 <sup>''</sup> )—C(6 <sup>''</sup> )—O(7 <sup>''</sup> )	107.9 (10)
O(3)—Ba(2 <sup>+</sup> )—O(9)	118.1 (3)	C(9 <sup>''</sup> )—C(8 <sup>''</sup> )—O(7 <sup>''</sup> )	112 (1)
O(3)—Ba(2 <sup>+</sup> )—O(12)	77.0 (3)	C(8 <sup>''</sup> )—C(9 <sup>''</sup> )—O(10 <sup>''</sup> )	109 (1)

hourly, 6.1% decrease was observed during the 92 h collection time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with  $30 < 2\theta < 32^\circ$ . Corrections for Lorentz and polarization effects were applied. The Ba- and Cl-atom positions were determined using the Patterson method. From a  $\Delta F$  synthesis the positions of the other non-H atoms were derived. After isotropic refinement a subsequent  $\Delta F$  synthesis revealed three peaks which were interpreted as acetonitrile, one of the solvents used in the crystallization of the compound. The positions of the H atoms were calculated. Block-diagonal least-squares refinement on  $F$  with anisotropic displacement parameters for the non-H atoms converged to  $R = 0.056$ ,  $wR = 0.094$ ,  $(\Delta/\sigma)_{\max} = 0.27$ . The H atoms were not stable during refinement, so they were kept fixed at their calculated positions with  $U = 0.06 \text{ \AA}^2$ .  $w = (20.0 + F_{\text{obs}}^2 + 0.029F_{\text{obs}}^2)^{-1}$ . An empirical absorption correction was applied, with corrections in the range 0.80–1.25 (*DIFABS*; Walker & Stuart, 1983). A final difference synthesis revealed residual electron density between  $-0.6$  and  $0.8 \text{ e \AA}^{-3}$ . Scattering factors were taken from Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Ba and 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 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')

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52352 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond in Fig. 2. A least-squares plane calculation shows that the acridinium group is nearly planar: the maximum distance of an atom from the plane is 0.037 Å. The phenyl ring is planar to within 0.013 Å. The angle between the two planes is  $79^\circ$ .

For the mean cavity radius, as defined by Mathieu, Metz, Moras & Weiss (1978), a value of 1.51 Å was obtained. The distance from the Ba ion to the centre

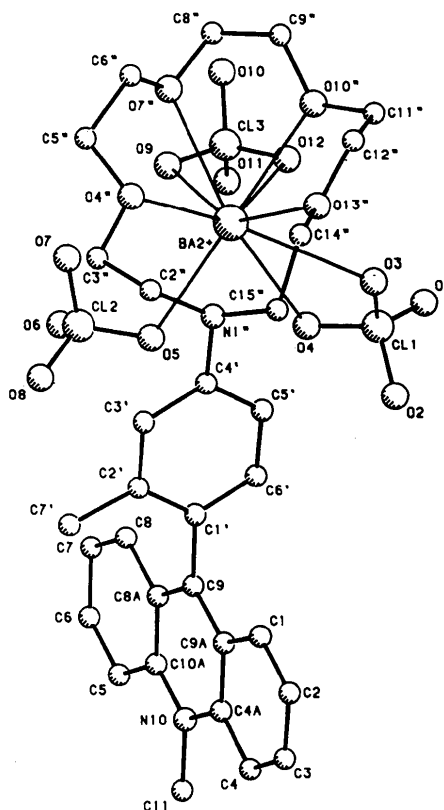


Fig. 1. Structure of  $[C_{31}H_{37}N_2O_4Ba(ClO_4)_3]$  showing the numbering scheme.

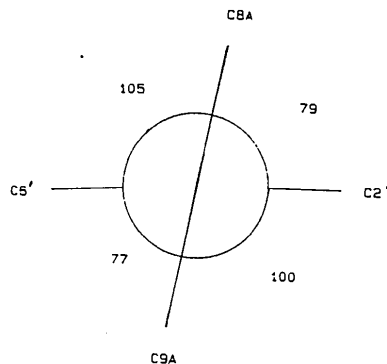


Fig. 2. The Newman projection along the C(9)—C(1') bond.

of gravity of the hetero atoms in the crown ether is 1.76 Å, the angle N(1'')-centre of gravity-Ba is 88°.

The O atoms of the crown ether deviate alternately about 0.08 Å above and below their mean plane; the N atom lies 1.063 Å below this plane.

The Ba ion is coordinated by the four O atoms of the crown ether and by the three perchlorate ions, one unidentate the others bidentate (distances about 3.0 Å). The distances from the Ba ion to the N atom in the crown ether and to the O(7) atom of the unidentate perchlorate are each about 3.3 Å. Thus, in analogy with the sixth structure in this series (Zoutberg *et al.*, 1989), it can be argued that the Ba ion is 11- rather than 9-coordinated.

#### 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.)
- GOUBITZ, K., REISS, C. A. & HEIJDENRIJK, D. (1989a). *Acta Cryst.* **C45**, 1356–1358.
- GOUBITZ, K., REISS, C. A. & HEIJDENRIJK, D. (1989b). *Acta Cryst.* **C45**, 1364–1366.
- GOUBITZ, K., REISS, C. A., HEIJDENRIJK, D., JONKER, S. A. & VERHOEVEN, J. W. (1989). *Acta Cryst.* **C45**, 1348–1350.
- KRONENBURG, M. J., GOUBITZ, K., REISS, C. A. & HEIJDENRIJK, D. (1989a). *Acta Cryst.* **C45**, 1352–1353.
- KRONENBURG, M. J., GOUBITZ, K., REISS, C. A. & HEIJDENRIJK, D. (1989b). *Acta Cryst.* **C45**, 1361–1363.
- MATHEU, 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.
- REISS, C. A., GOUBITZ, K. & HEIJDENRIJK, D. (1989a). *Acta Cryst.* **C45**, 1350–1352.
- REISS, C. A., GOUBITZ, K. & HEIJDENRIJK, D. (1989b). *Acta Cryst.* **C45**, 1354–1356.
- REISS, C. A., GOUBITZ, K., ZOUTBERG, M. C. & HEIJDENRIJK, D. (1989). *Acta Cryst.* **C45**, 1366–1369.
- 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.
- ZOUTBERG, M. C., REISS, C. A., GOUBITZ, K. & HEIJDENRIJK, D. (1989). *Acta Cryst.* **C45**, 1359–1361.

*Acta Cryst.* (1990). **C46**, 465–467

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

BY CELESTE A. REISS, KEES GOUBITZ AND DICK HEIJDENRIJK

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

(Received 25 April 1989; accepted 15 June 1989)

**Abstract.**  $C_{31}H_{37}N_2O_4^+ \cdot Li^+ \cdot 2ClO_4^-$ ,  $M_r = 707.5$ , orthorhombic, *Pbca*,  $a = 13.064$  (1),  $b = 15.940$  (2),  $c = 31.575$  (4) Å,  $V = 6575$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.43$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 23.5$  cm<sup>-1</sup>,  $F(000) = 2960$ , room temperature. Final  $R = 0.082$  for 2259 observed reflections. The angle between the planes of the acridinium and the phenyl groups is 66°. The Li atom is coordinated by the four O atoms of the crown ether [1.99 (2)–2.20 (2) Å] and by one O atom of one of the perchlorate ions [1.99 (2) Å].

**Introduction.** This paper is the eleventh in our series of structural studies of acridinium dyes (I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeven, 1989; II, IV: Reiss, Goubitz & Heijdenrijk, 1989a,b; III, VII: Kronenburg, Goubitz, Reiss & Heijdenrijk, 1989a,b; V, VIII: Goubitz, Reiss & Heijdenrijk, 1989a,b; VI: Zoutberg, Reiss, Goubitz & Heijdenrijk, 1989; IX: Reiss, Goubitz, Zoutberg & Heijdenrijk, 1989; X: Häming, Reiss, Goubitz & Heijdenrijk, 1989). In this

case the phenyl ring is substituted with both a methyl group and an aza[15]crown-5 group which has formed a complex with lithium perchlorate.

**Experimental.** A dark-brown plate-shaped crystal (dimensions 0.03 × 0.35 × 0.35 mm approximately) was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu  $K\alpha$  radiation and  $\omega$ -2 $\theta$  scans. A total of 4089 unique reflections was measured within the range  $0 \leq h \leq 13$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 33$ . Of these, 2259 were above the significance level of  $2.5 \sigma(I)$ . The maximum value of  $(\sin \theta)/\lambda$  was  $0.53$  Å<sup>-1</sup>. Two standard reflections (213, 004) were measured hourly, no significant decrease was observed during the 46 h collection time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with  $49 < 2\theta < 54^\circ$ . Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods using the program