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Crystal Studies of Acridinium Dyes. IV. Two Modifications of 9-(4-Hydroxyphenyl)-10-methylacridinium Chloride

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Abstract. $C_{20}H_{16}NO^+.Cl^-$, $M_r = 321·8$. (*A*): triclinic, $P\bar{1}$, $a = 10·478\ (1)$, $b = 12·371\ (1)$, $c = 6·646\ (1)$ Å, $\alpha = 99·69\ (1)$, $\beta = 95·17\ (1)$, $\gamma = 109·08\ (1)°$, $V = 792·7\ (2)$ Å^3, $Z = 2$, $D_x = 1·35$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 21·7$ cm^{-1}, $F(000) = 336$, room temperature. Final $R = 0·041$ for 2111 observed reflections. (*B*): monoclinic, $P2_1/n$, $a = 12·3467\ (6)$, $b = 23·8531\ (12)$, $c = 5·4109\ (5)$ Å, $\beta = 93·977\ (5)°$, $V = 1589·7\ (2)$ Å^3, $Z = 4$, $D_x = 1·35$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 21·6$ cm^{-1}, $F(000) = 672$, room temperature. Final $R = 0·047$ for 1926 observed reflections. The acridinium moiety is less planar in (*B*) than in (*A*). The phenyl rings are planar in both compounds. The angle between the acridinium and the phenyl groups is 63° in (*A*) and 70° in (*B*).

Introduction. The title compound is the fourth structure in a series of acridinium dyes [I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeven (1989); II: Reiss, Goubitz & Heijdenrijk (1989); III: Kronenburg, Goubitz, Reiss & Heijdenrijk (1989)]. In this case the phenyl ring is substituted with a hydroxy group. The structure crystallizes in two modifications, a triclinic (*A*) and a monoclinic (*B*) form.

Experimental. *Modification* (*A*): An orange plate-shaped crystal (dimensions $0·04 \times 0·20 \times 0·40$ 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 2684 unique reflections was measured within the range $-12 \le h \le 12$, $-14 \le k \le 13$, $-1 \le l \le 7$. Of these, 2111 were above the significance level of $2·5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·59 Å^{-1}. Two standard reflections ($20\bar{1}$, $3\bar{2}1$) were measured hourly, the intensity showed no significant decrease during the 30 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $60 < 2\theta < 71°$. 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 $R = 0·041$, $wR = 0·054$, $(\Delta/\sigma)_{\max} = 0·14$. A weighting scheme $w = (6·22 + F_{\text{obs}} + 0·009F^2_{\text{obs}})^{-1}$ was used. An empirical absorption correction was applied, with corrections in the range 0·73–1·30 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between $-0·2$ and $0·2$ e Å^{-3}.

Modification (*B*): A dark-yellow plate-shaped crystal (dimensions $0·01 \times 0·30 \times 0·40$ 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 2710 unique reflections was measured within the range $-14 \le h \le 14$, $0 \le k \le 27$, $0 \le l \le 6$. Of these, 1926 were above the significance level of $2·5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·59 Å^{-1}. Two standard reflections (040, 111) were measured hourly, the intensity showed no significant decrease during the 30 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $79 < 2\theta < 90°$.

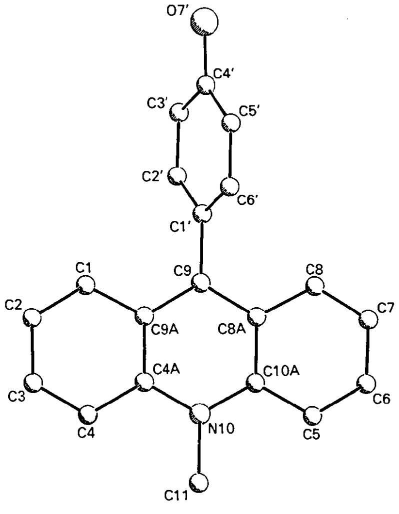

Fig. 1. Structure of $[C_{20}H_{16}NO]^+$, modification (*A*), showing the numbering scheme.

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

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

	x	y	z	U_{eq}(Å^2)
Modification (*A*)				
Cl	0·13248 (7)	0·36488 (6)	0·8178 (1)	0·0578 (4)
C(1)	−0·5572 (3)	−0·1511 (2)	0·0364 (4)	0·046 (1)
C(2)	−0·6659 (3)	−0·1719 (2)	−0·1110 (4)	0·051 (1)
C(3)	−0·7900 (3)	−0·2607 (2)	−0·1112 (4)	0·052 (1)
C(4)	−0·8042 (2)	−0·3285 (2)	0·0327 (4)	0·047 (1)
C(5)	−0·6133 (3)	−0·4334 (2)	0·6305 (4)	0·054 (2)
C(6)	−0·5019 (4)	−0·4205 (3)	0·7664 (4)	0·064 (2)
C(7)	−0·3732 (3)	−0·3396 (3)	0·7675 (4)	0·058 (2)
C(8)	−0·3568 (3)	−0·2661 (2)	0·6328 (4)	0·048 (1)
C(9)	−0·4546 (2)	−0·1987 (2)	0·3471 (3)	0·036 (1)
C(11)	−0·8442 (3)	−0·4613 (3)	0·3390 (5)	0·061 (2)
N(10)	−0·7078 (2)	−0·3749 (2)	0·3376 (3)	0·040 (1)
C(4a)	−0·6926 (2)	−0·3094 (2)	0·1873 (4)	0·038 (1)
C(8a)	−0·4699 (2)	−0·2740 (2)	0·4876 (3)	0·039 (1)
C(9a)	−0·5657 (2)	−0·2201 (2)	0·1907 (3)	0·037 (1)
C(10a)	−0·5992 (3)	−0·3611 (2)	0·4836 (3)	0·041 (1)
O(7′)	0·0333 (2)	0·1842 (2)	0·4236 (3)	0·062 (1)
C(1′)	−0·3256 (2)	−0·0982 (2)	0·3681 (4)	0·040 (1)
C(2′)	−0·2433 (3)	−0·0885 (2)	0·2144 (4)	0·049 (1)
C(3′)	−0·1239 (3)	0·0054 (2)	0·2375 (4)	0·053 (1)
C(4′)	−0·0832 (2)	0·0929 (2)	0·4146 (4)	0·045 (1)
C(5′)	−0·1631 (3)	0·0847 (2)	0·5696 (4)	0·047 (1)
C(6′)	−0·2827 (2)	−0·0108 (2)	0·5470 (4)	0·045 (1)
Modification (*B*)				
Cl	0·22637 (7)	0·20805 (4)	0·6188 (2)	0·0459 (4)
C(1)	−0·0859 (2)	0·1195 (1)	1·0032 (6)	0·034 (2)
C(2)	−0·0215 (3)	0·1517 (1)	0·8655 (7)	0·041 (2)
C(3)	−0·0676 (3)	0·1908 (1)	0·6973 (7)	0·045 (2)
C(4)	−0·1767 (3)	0·1994 (1)	0·6670 (6)	0·041 (2)
C(5)	−0·5345 (3)	0·1661 (2)	0·9599 (7)	0·044 (2)
C(6)	−0·5973 (3)	0·1415 (2)	1·1245 (8)	0·052 (2)
C(7)	−0·5564 (3)	0·1001 (2)	1·2881 (7)	0·052 (2)
C(8)	−0·4512 (3)	0·0826 (2)	1·2807 (7)	0·045 (2)
C(9)	−0·2701 (2)	0·0936 (1)	1·1181 (5)	0·030 (1)
C(11)	−0·4038 (3)	0·2181 (1)	0·6123 (7)	0·047 (2)
N(10)	−0·3571 (2)	0·1771 (1)	0·7946 (5)	0·033 (1)
C(4a)	−0·2466 (2)	0·1684 (1)	0·8142 (5)	0·032 (2)
C(8a)	−0·3809 (2)	0·1082 (1)	1·1139 (6)	0·034 (2)
C(9a)	−0·2014 (2)	0·1269 (1)	0·9828 (5)	0·030 (2)
C(10a)	−0·4234 (2)	0·1510 (1)	0·9529 (6)	0·034 (2)
O(7′)	−0·1347 (2)	−0·10238 (10)	1·6330 (5)	0·051 (1)
C(1′)	−0·2309 (2)	0·0426 (1)	1·2535 (6)	0·033 (2)
C(2′)	−0·1612 (3)	0·0446 (1)	1·4667 (6)	0·038 (2)
C(3′)	−0·1299 (3)	−0·0039 (1)	1·5923 (6)	0·041 (2)
C(4′)	−0·1663 (3)	−0·0559 (1)	1·5036 (6)	0·036 (2)
C(5′)	−0·2329 (3)	−0·0580 (1)	1·2871 (7)	0·042 (2)
C(6′)	−0·2669 (3)	−0·0099 (1)	1·1668 (6)	0·040 (2)

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 $R = 0{\cdot}047$, $wR = 0{\cdot}065$, $(\Delta/\sigma)_{max} = 0{\cdot}27$. A weighting scheme $w = (7{\cdot}04 + F_{obs} + 0{\cdot}011F_{obs}^2)^{-1}$ was used. The isotropic secondary-extinction coefficient refined to $5{\cdot}7\,(7) \times 10^{-4}$ (Zachariasen, 1968). An empirical absorption correction was applied, with corrections in the range 0·83–1·21 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between −0·1 and 0·2 e Å^{-3}.

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

	(*A*)	(*B*)		(*A*)	(*B*)
C(1)—C(2)	1·358 (3)	1·364 (3)	C(11)—N(10)	1·481 (3)	1·477 (3)
C(1)—C(9a)	1·432 (2)	1·434 (3)	N(10)—C(4a)	1·377 (2)	1·377 (3)
C(2)—C(3)	1·401 (3)	1·397 (4)	N(10)—C(10a)	1·372 (2)	1·374 (3)
C(3)—C(4)	1·362 (3)	1·361 (4)	C(4a)—C(9a)	1·419 (3)	1·433 (3)
C(4)—C(4a)	1·414 (3)	1·422 (3)	C(8a)—C(10a)	1·424 (3)	1·419 (3)
C(5)—C(6)	1·358 (3)	1·354 (4)	O(7′)—C(4′)	1·354 (2)	1·354 (3)
C(5)—C(10a)	1·417 (3)	1·421 (3)	C(1′)—C(2′)	1·391 (3)	1·391 (3)
C(6)—C(7)	1·391 (4)	1·397 (4)	C(1′)—C(6′)	1·392 (3)	1·399 (3)
C(7)—C(8)	1·363 (3)	1·368 (4)	C(2′)—C(3′)	1·376 (3)	1·383 (3)
C(8)—C(8a)	1·425 (3)	1·432 (3)	C(3′)—C(4′)	1·385 (3)	1·393 (3)
C(9)—C(8a)	1·410 (2)	1·410 (3)	C(4′)—C(5′)	1·381 (3)	1·385 (3)
C(9)—C(9a)	1·412 (2)	1·404 (3)	C(5′)—C(6′)	1·388 (3)	1·371 (3)
C(9)—C(1′)	1·484 (2)	1·484 (3)			

	(*A*)	(*B*)
C(2)—C(1)—C(9a)	121·2 (2)	120·2 (2)
C(1)—C(2)—C(3)	120·0 (2)	120·4 (3)
C(2)—C(3)—C(4)	121·3 (2)	122·3 (3)
C(3)—C(4)—C(4a)	120·0 (2)	119·2 (3)
C(6)—C(5)—C(10a)	119·1 (2)	120·4 (3)
C(5)—C(6)—C(7)	122·9 (3)	121·6 (3)
C(6)—C(7)—C(8)	119·6 (3)	120·0 (3)
C(7)—C(8)—C(8a)	120·3 (2)	120·5 (3)
C(8a)—C(9)—C(9a)	118·3 (2)	118·2 (2)
C(8a)—C(9)—C(1′)	120·2 (2)	119·6 (2)
C(9a)—C(9)—C(1′)	121·4 (2)	122·2 (2)
C(11)—N(10)—C(4a)	118·7 (2)	119·3 (2)
C(11)—N(10)—C(10a)	120·3 (2)	119·6 (2)
C(4a)—N(10)—C(10a)	121·1 (2)	120·9 (2)
C(4)—C(4a)—N(10)	120·2 (2)	121·0 (2)
C(4)—C(4a)—C(9a)	119·8 (2)	119·4 (2)
N(10)—C(4a)—C(9a)	120·0 (2)	119·6 (2)
C(8)—C(8a)—C(9)	121·0 (2)	121·0 (2)
C(8)—C(8a)—C(10a)	118·9 (2)	118·6 (3)
C(9)—C(8a)—C(10a)	120·1 (2)	120·3 (2)
C(1)—C(9a)—C(9)	122·1 (2)	121·6 (2)
C(1)—C(9a)—C(4a)	117·7 (2)	118·4 (2)
C(9)—C(9a)—C(4a)	120·2 (2)	120·0 (2)
C(5)—C(10a)—N(10)	120·9 (2)	121·3 (2)
C(5)—C(10a)—C(8a)	119·1 (2)	118·8 (2)
N(10)—C(10a)—C(8a)	120·0 (2)	119·8 (2)
C(9)—C(1′)—C(2′)	122·0 (2)	122·9 (2)
C(9)—C(1′)—C(6′)	120·0 (2)	118·9 (2)
C(2′)—C(1′)—C(6′)	118·0 (2)	118·2 (2)
C(1′)—C(2′)—C(3′)	121·0 (2)	121·0 (2)
C(2′)—C(3′)—C(4′)	120·6 (2)	120·2 (3)
O(7′)—C(4′)—C(3′)	117·2 (2)	118·4 (3)
O(7′)—C(4′)—C(5′)	123·4 (2)	122·7 (2)
C(3′)—C(4′)—C(5′)	119·4 (2)	118·8 (3)
C(4′)—C(5′)—C(6′)	119·9 (2)	121·1 (3)
C(1′)—C(6′)—C(5′)	121·1 (2)	120·7 (3)

For both modifications: 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, Machin, Dickinson, Ammon, Heck & Flack, 1976), unless stated otherwise.*

Discussion. Final positional parameters for the non-H atoms for both modifications are listed in

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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 51848 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

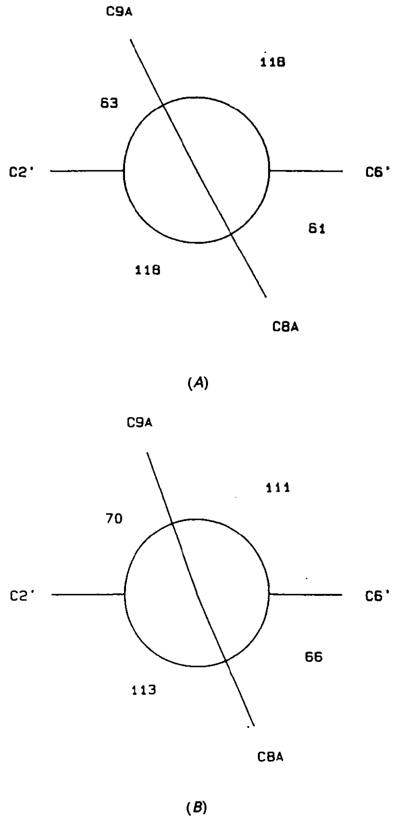

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

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. $C_{30}H_{35}N_2O_4^+.ClO_4^-$, $M_r = 587·1$, monoclinic, $P2_1/n$, $a = 23·639\ (1)$, $b = 12·659\ (1)$, $c = 9·740\ (1)$ Å, $\beta = 90·316\ (6)°$, $V = 2914·6\ (4)$ Å^3, $Z = 4$, $D_x = 1·34$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 16·0$ cm^{-1}, $F(000) = 1144$, room temperature. Final $R = 0·066$ 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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