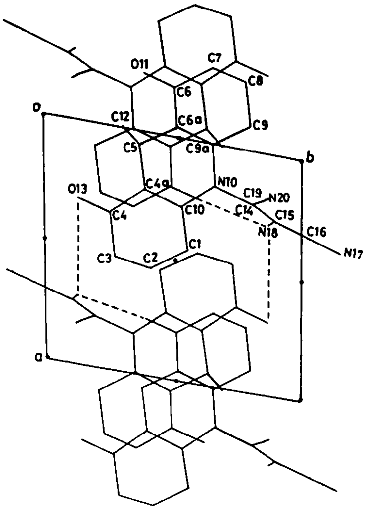

Fig. 2. The packing of the molecule in the projection of the c axis.

The dihedral angle between the least-squares planes of the dicyano group and the acridinyl ring is 92·6 (8)°. N(18) is involved in two hydrogen bonds N(18)···O(11) and N(18)···O(13) with distances and angles 2·84 (3), 2·81 (3) Å and 142 (2), 130 (2)° respectively, and H′(18)···O(11) and H″(18)···O(13) distances 1·93 and 2·00 Å respectively (symmetry: $-x, -y+1, -z+2$ and $x, y+1, z$). The packing of the molecule is stabilized by the hydrogen-bonding scheme and the van der Waals forces.

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Crystal Studies of Acridinium Dyes. I. 10-Methyl-9-phenylacridinium Chloride Hydrate

By Kees Goubitz, Celeste A. Reiss and Dick Heijdenrijk

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

and Stephan A. Jonker and Jan W. Verhoeven

Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, *Amsterdam, The Netherlands*

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Abstract. $C_{20}H_{16}N^+.Cl^-.H_2O$, $M_r = 323{\cdot}8$, triclinic, $P\bar{1}$, $a = 11{\cdot}0409\ (7)$, $b = 15{\cdot}2215\ (10)$, $c = 5{\cdot}1772\ (4)$ Å, $\alpha = 97{\cdot}599\ (9)$, $\beta = 96{\cdot}633\ (9)$, $\gamma = 108{\cdot}026\ (6)°$, $V = 808{\cdot}7\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}33$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 21{\cdot}2$ cm^{-1}, $F(000) = 340$, room temperature. Final $R = 0{\cdot}058$ for 2340 observed reflections. The angle between the acridinium and the phenyl groups is 68°. The acridinium moiety is planar, the maximum distance from the plane is 0·070 Å for C(9).

Introduction. 10-Methyl-9-phenylacridinium chloride is the basic structure of a group of acridinium dyes with interesting photophysical properties. These properties, as well as their electrochemical behaviour (Koper, Jonker & Verhoeven, 1985) are strongly influenced by the presence of substituents on the phenyl group (Jonker, Ariese & Verhoeven, 1989). This influence is mainly due to the steric effect of the substituents on the twist angle between the planes of the acridinium and the phenyl groups. In order to

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

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

	x	y	z	U_{eq}(Å^2)
Cl	0·35449 (10)	0·11664 (8)	0·0745 (2)	0·0517 (5)
C(1)	0·9404 (4)	0·3584 (3)	0·3089 (7)	0·041 (2)
C(2)	0·8432 (4)	0·3642 (3)	0·4408 (8)	0·046 (2)
C(3)	0·7180 (4)	0·3005 (3)	0·3572 (8)	0·047 (2)
C(4)	0·6909 (3)	0·2318 (3)	0·1398 (8)	0·044 (2)
C(5)	0·8369 (4)	0·0697 (3)	−0·5696 (8)	0·047 (2)
C(6)	0·9344 (4)	0·0613 (3)	−0·6982 (8)	0·050 (2)
C(7)	1·0616 (4)	0·1238 (3)	−0·6241 (8)	0·048 (2)
C(8)	1·0887 (4)	0·1953 (3)	−0·4165 (8)	0·042 (2)
C(9)	1·0174 (3)	0·2826 (2)	−0·0616 (6)	0·033 (2)
C(11)	0·6314 (4)	0·0907 (3)	−0·3198 (9)	0·055 (2)
N(10)	0·7659 (3)	0·1551 (2)	−0·2205 (6)	0·036 (1)
C(4a)	0·7896 (3)	0·2241 (2)	−0·0066 (7)	0·036 (2)
C(8a)	0·9913 (3)	0·2078 (2)	−0·2711 (6)	0·033 (2)
C(9a)	0·9171 (3)	0·2887 (2)	0·0784 (7)	0·035 (2)
C(10a)	0·8624 (3)	0·1436 (2)	−0·3515 (7)	0·037 (2)
O(1s)	1·4419 (4)	0·2531 (3)	−0·3576 (7)	0·075 (2)
C(1′)	1·1474 (3)	0·3550 (2)	0·0158 (7)	0·036 (2)
C(2′)	1·1632 (4)	0·4471 (3)	−0·0191 (7)	0·043 (2)
C(3′)	1·2820 (4)	0·5164 (3)	0·0608 (8)	0·050 (2)
C(4′)	1·3858 (4)	0·4957 (3)	0·1801 (8)	0·055 (2)
C(5′)	1·3714 (4)	0·4045 (3)	0·2094 (9)	0·056 (2)
C(6′)	1·2533 (4)	0·3343 (3)	0·1279 (8)	0·045 (2)

obtain quantitative information about this effect an X-ray investigation of a series of variously substituted phenyl acridinium compounds was undertaken.

Experimental. A bright yellow plate-shaped crystal (dimensions 0·10 × 0·18 × 0·23 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 3029 unique reflections was measured within the range $-12 \le h \le 12$, $-17 \le k \le 17$, $-6 \le l \le 5$. Of these, 2340 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·61 Å^{-1}. Two standard reflections (210, $1\bar{2}1$) were measured hourly, the intensity decrease was 6·5% during the 34 h collection time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $60 < 2\theta < 80°$. Corrections for Lorentz and polarization effects were applied. The structure was determined by direct methods with the program *SIMPEL* (Schenk & Kiers, 1985). From a ΔF synthesis the water molecule and 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 $R =$ 0·058, $wR = 0{\cdot}088$, $(\Delta/\sigma)_{\max} = 0{\cdot}50$. A weighting scheme $w = (5{\cdot}96 + F_{\text{obs}} + 0{\cdot}084F_{\text{obs}}^2)^{-1}$ was used. The isotropic secondary-extinction coefficient refined to 2·7 (5) × 10^{-4} (Zachariasen, 1968). An empirical absorption correction was applied, with corrections in the range 0·73–1·28 (*DIFABS*; Walker & Stuart, 1983). A final difference Fourier map revealed a residual electron density between −0·2 and 0·5 e Å^{-3}. Scattering factors were taken from

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

C(1)—C(2)	1·356 (6)	C(9)—C(1′)	1·485 (4)
C(1)—C(9a)	1·429 (5)	C(11)—C(10)	1·490 (4)
C(2)—C(3)	1·400 (5)	N(10)—C(4a)	1·361 (4)
C(3)—C(4)	1·366 (5)	C(10)—C(10a)	1·370 (5)
C(4)—C(4a)	1·422 (6)	C(4a)—C(9a)	1·424 (4)
C(5)—C(6)	1·359 (7)	C(8a)—C(10a)	1·431 (4)
C(5)—C(10a)	1·419 (5)	C(1′)—C(2′)	1·397 (6)
C(6)—C(7)	1·406 (5)	C(1′)—C(6′)	1·387 (6)
C(7)—C(8)	1·358 (5)	C(2′)—C(3′)	1·381 (5)
C(8)—C(8a)	1·427 (6)	C(3′)—C(4′)	1·380 (7)
C(9)—C(8a)	1·398 (4)	C(4′)—C(5′)	1·378 (7)
C(9)—C(9a)	1·411 (5)	C(5′)—C(6′)	1·383 (5)

C(2)—C(1)—C(9a)	120·9 (3)	C(8)—C(8a)—C(9)	121·9 (3)
C(1)—C(2)—C(3)	120·6 (4)	C(8)—C(8a)—C(10a)	118·4 (3)
C(2)—C(3)—C(4)	120·8 (4)	C(9)—C(8a)—C(10a)	119·7 (3)
C(3)—C(4)—C(4a)	120·4 (3)	C(1)—C(9a)—C(9)	121·4 (3)
C(6)—C(5)—C(10a)	119·7 (3)	C(1)—C(9a)—C(4a)	118·3 (3)
C(5)—C(6)—C(7)	122·4 (4)	C(9)—C(9a)—C(4a)	120·3 (3)
C(6)—C(7)—C(8)	119·1 (4)	C(5)—C(10a)—N(10)	121·2 (3)
C(7)—C(8)—C(8a)	121·5 (3)	C(5)—C(10a)—C(8a)	118·9 (4)
C(8a)—C(9)—C(9a)	118·7 (3)	N(10)—C(10a)—C(8a)	119·8 (3)
C(8a)—C(9)—C(1′)	121·6 (3)	C(9)—C(1′)—C(2′)	119·3 (3)
C(9a)—C(9)—C(1′)	119·7 (3)	C(9)—C(1′)—C(6′)	121·8 (3)
C(11)—N(10)—C(4a)	119·7 (3)	C(2′)—C(1′)—C(6′)	118·9 (3)
C(11)—N(10)—C(10a)	118·4 (3)	C(1′)—C(2′)—C(3′)	120·3 (4)
C(4a)—N(10)—C(10a)	121·9 (3)	C(2′)—C(3′)—C(4′)	120·3 (4)
C(4)—C(4a)—N(10)	121·7 (3)	C(3′)—C(4′)—C(5′)	119·5 (3)
C(4)—C(4a)—C(9a)	118·9 (3)	C(4′)—C(5′)—C(6′)	120·7 (4)
N(10)—C(4a)—C(9a)	119·4 (3)	C(1′)—C(6′)—C(5′)	120·2 (4)

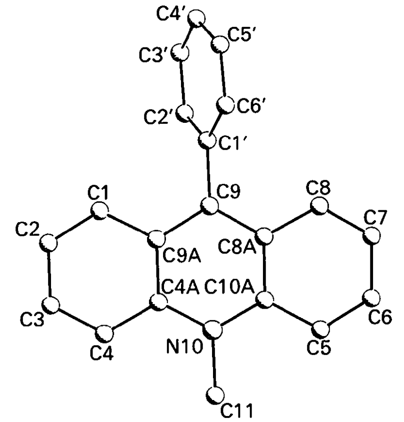

Fig. 1. Structure of $[C_{20}H_{16}N]^+$ showing the numbering scheme.

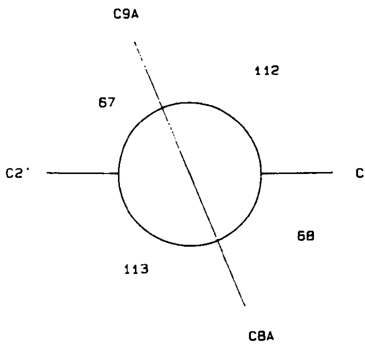

Fig. 2. The Newman projection along the C(9)—C(1′) bond.

Cromer & Mann (1968); *International Tables for X-ray Crystallography* (1974). Anomalous dispersion for Cl was corrected for. All calculations were performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 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′) bond in Fig. 2. A least-squares plane through the acridinium atoms shows that the maximum distance from the plane is 0·070 Å [C(9)]. N(10) lies 0·055 Å from the plane, all other distances are less than 0·048 Å. The phenyl ring is planar {max. distance from the best plane is 0·014 Å [C(4′)]}. The angle between the least-squares planes through these moieties is 68°.

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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 51845 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystal Studies of Acridinium Dyes. II. 9-(4-Dimethylamino-2-methylphenyl)-10-methylacridinium Chloride Dihydrate

By Celeste A. Reiss, Kees Goubitz and Dick Heijdenrijk

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

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Abstract. $C_{23}H_{23}N_2^+.Cl^-.2H_2O$, $M_r = 398{\cdot}9$, triclinic, $P\bar{1}$, $a = 9{\cdot}3079$ (6), $b = 12{\cdot}9187$ (9), $c = 9{\cdot}1687$ (6) Å, $\alpha = 107{\cdot}577$ (10), $\beta = 91{\cdot}752$ (7), $\gamma = 86{\cdot}121$ (7)°, $V = 1048{\cdot}6$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}26$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 16{\cdot}6$ cm^{-1}, $F(000) = 424$, room temperature. Final $R = 0{\cdot}063$ for 2698 observed reflections. The acridinium group and the phenyl ring are each nearly planar. The angle between the acridinium plane and the phenyl ring is 72°. There are no unusual bond lengths or angles.

Introduction. The title compound is the second structure in a series of acridinium dyes [I: Goubitz, Reiss, Heijdenrijk, Jonker & Verhoeyen (1989)]. In the structure here presented the phenyl ring is substituted with a methyl and a dimethylamino group.

Experimental. A blue-purple plate-shaped crystal (dimensions 0·08 × 0·38 × 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 3963 unique reflections was measured within the range $-11 \le h \le 11$, $-15 \le k \le 15$, $0 \le l \le 11$. Of these, 2698 were above the significance level of $2{\cdot}5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0·61 Å^{-1}. Two standard reflections ($\overline{2}\overline{2}1$, 002) were measured hourly, the intensity decrease was 5·1% during the 45 h collecting time. Unit-cell parameters were refined by a least-squares-fitting procedure using 23 reflections with $70 < 2\theta < 80°$. 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 water molecules and the H atoms were derived. Block-diagonal least-squares refinement on F, anisotropic for the non-H and isotropic for the H atoms, converged to $R = 0{\cdot}063$,

0108-2701/89/091350-03$03.00