

FORMATION OF QUINOACRIDINIUM SYSTEM.
A NOVEL REACTION OF QUINALDINIUM SALTS

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Abstract - N-Ethylquinaldinium salts heated in a solvent in the presence of a secondary amine yield 8,13-diethyl-6-methyl-8H-quino[4,3,2-de]acridinium salts. The structure of the iodide is determined by X-ray analysis. It is found that bond distances in quinoacridinium system are strongly affected by resonance interactions.

In the course of our studies on cyanine dye formation we have found that if syntheses using N-alkylquinaldinium salts are carried out in the presence of a strongly basic secondary amine, such as piperidine or pyrrolidine, instead of the commonly used sodium or potassium hydroxide, several coloured products are formed in considerable amounts in addition to the required cyanine.¹ The distribution of these products depends on the substrate as well as on the reaction conditions.

In this paper a novel reaction of N-ethylquinaldinium iodide in the presence of piperidine is reported and the structure of the reaction product, as determined by X-ray analysis, is described.

RESULTS

We have found that N-ethylquinaldinium iodide heated in ethanol with an equimolar amount of piperidine yields as the main product (over 60%) an intensely red crystalline compound which, according to elemental analysis, might have the same formula as pseudocyanine iodide. However, its UV-VIS spectrum (Fig. 1) indicated that there were considerable differences in their structures.

Both ¹H and ¹³C NMR spectra indicated that the compound contained 19 carbon atoms in a heteroaromatic system and a methyl group. Thus it was evident that two molecules of quinaldinium iodide had taken part in the reaction. The number of quaternary carbon atoms (9 according to the off-resonance spectrum) indicated that in reaction a novel ring closure had occurred.

To determine the structure of the reaction product an X-ray analysis was undertaken. The compound was thus identified as 8,13-diethyl-6-methyl-8H-quinol[4,3,2-de]acridinium iodide.

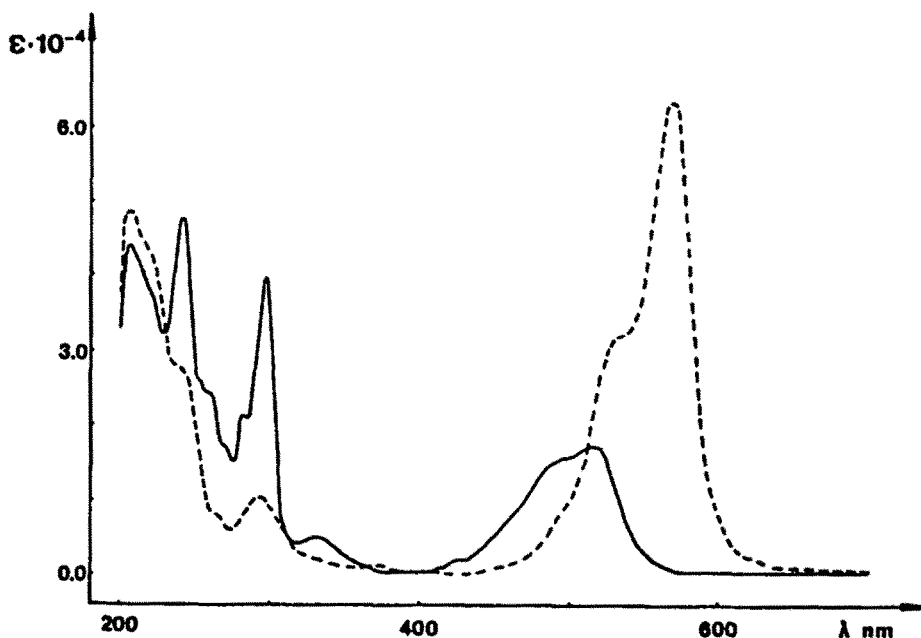


Fig. 1. UV-VIS spectrum of 8,13-diethyl-6-methyl-8H-quinol[4,3,2-de]acridinium iodide (full line) and pseudocyanine iodide (dotted line).

The structure of the product shows that it is formed in a multistep reaction as a result of ring opening at the C2-N bond of one of the molecules of N-ethylquinolindinium iodide and two ring closures. The reaction requires cleavage of 6 bonds, one C-N and five C-H, the formation of 4 new bonds: one double and two single ones, and removal of five hydrogen atoms. The reaction sequence needs clarification. It remains unclear how the hydrogen atoms are removed, but it seems probable that another molecule of the quinolindinium salt might serve as the acceptor of hydrogen atoms, and in further reactions decompose to tar.

STRUCTURE

The shape of the cation with the numbering system is shown in Fig. 2 and torsion angles in Fig. 3. Bond lengths and angles are given in Table 1 and Table 2. The bond lengths are generally those expected from consideration of the 18 resonance forms with the positive charge located at N(18) or N(13). The C-C and C-N bond lengths in the ring system are in the range 1.36(1) - 1.47(1) and 1.36(1) - 1.40(1) Å respectively. The longest bond is between C(4A) and C(4B); only two of above mentioned 18 resonance forms have a double bond at this position.

Substitution of N(13) with the ethyl group results in overcrowding between C(12) and C(17). Analogously to overcrowded regions in polycyclic aromatic

hydrocarbons, we can refer to it as "the bay region". In hydrocarbons the overcrowding is relieved mainly by bond torsions, with the planar distribution of bonds around C atoms preserved.² The presence of a more easily deformable N atom in the "bay region" introduces an additional way to relieve the strain. The nitrogen N(13) atom in the "bay region" shows a slightly pyramidal configuration of bonds and is at a distance 0.103(1) Å from the plane through C(17), C(13A) and C(12B). However, as in polycyclic hydrocarbons, bond torsions also give rise to ring buckling. While for the planar conformation torsion angles should be 0° or 180°, in the "bay region" values as high as -16(1)° are observed (Fig. 3).

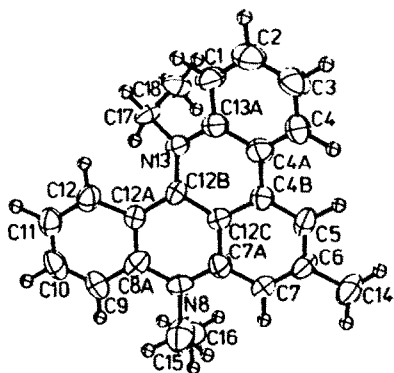


Fig. 2. View of the cation showing the atomic numbering

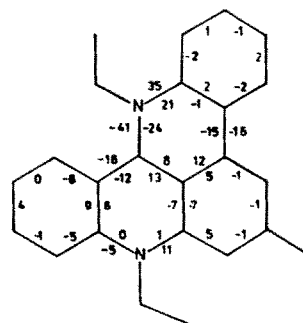


Fig. 3. Torsion angles in the cation system

Another overcrowded region in the cation lies between C(4) and C(5). Here the strain is mainly relieved by torsion ψ C(4) - C(4A) - C(4B) - C(5) = -16(1)°, and distortion of valence angles from the typical 120° values, so that finally the H atoms connected to C(4) and C(5) are 2.1 Å apart.

The crystal packing is shown in Fig. 4 and intermolecular distances are given in Table 3. In addition to the cation and anion there are two chloroform molecules in the asymmetric part of the unit cell. One of the chloroform molecules is disordered between two possible orientations occupied with 1:1 proportion. The C atoms of the chloroform molecules have close contacts with the I⁻ ion (Table 3).

All distances between the anion and cation are longer than 4 Å. There is a considerable overlap of the system of two symmetry-related cation (inversion centre at 1/2 1/2 0).

Table 1. Bond distances (\AA).

C(1) - C(2)	1.37(1)	C(6) - C(14)	1.50(1)	C(11) - C(12)	1.36(1)
C(2) - C(3)	1.37(1)	C(7) - C(7A)	1.42(1)	C(12) - C(12A)	1.43(1)
C(3) - C(4)	1.38(1)	C(7A) - N(8)	1.36(1)	C(12A) - C(12B)	1.41(1)
C(4) - C(4A)	1.39(1)	C(7A) - C(12C)	1.43(1)	C(12B) - C(12C)	1.42(1)
C(4A) - C(4B)	1.47(1)	N(8) - C(8A)	1.40(1)	C(12B) - N(13)	1.36(1)
C(4A) - C(13A)	1.42(1)	N(8) - C(15)	1.55(1)	N(13) - C(13A)	1.40(1)
C(4B) - C(5)	1.40(1)	C(8A) - C(9)	1.40(1)	N(13) - C(17)	1.50(1)
C(4B) - C(12C)	1.40(1)	C(8A) - C(12A)	1.44(1)	C(15) - C(16)	1.43(1)
C(5) - C(6)	1.40(1)	C(9) - C(10)	1.36(1)	C(17) - C(18)	1.51(1)
C(6) - C(7)	1.36(1)	C(10) - C(11)	1.40(1)		

Table 2. Bond angles ($^\circ$).

C(2) - C(1) - C(13A)	121(1)	C(9) - C(8A) - C(12A)	121(1)
C(1) - C(2) - C(3)	121(1)	C(8A) - C(9) - C(10)	120(1)
C(2) - C(3) - C(4)	120(1)	C(9) - C(10) - C(11)	121(1)
C(3) - C(4) - C(4A)	122(1)	C(10) - C(11) - C(12)	120(1)
C(4) - C(4A) - C(4B)	125(1)	C(11) - C(12) - C(12A)	122(1)
C(4) - C(4A) - C(13A)	118(1)	C(12) - C(12A) - C(12B)	123(1)
C(4B) - C(4A) - C(13A)	116.8(9)	C(12) - C(12A) - C(8A)	115.8(9)
C(4A) - C(4B) - C(5)	122.1(9)	C(12B) - C(12A) - C(8A)	121.0(9)
C(5) - C(4B) - C(12C)	120(1)	C(12A) - C(12B) - C(12C)	118.1(9)
C(4A) - C(4B) - C(12C)	117.7(9)	N(13) - C(12B) - C(12A)	123.2(8)
C(4B) - C(5) - C(6)	120(1)	N(13) - C(12B) - C(12C)	118.7(9)
C(5) - C(6) - C(7)	121(1)	C(12B) - C(12C) - C(4B)	121.0(9)
C(5) - C(6) - C(14)	119(1)	C(12B) - C(12C) - C(7A)	119.7(9)
C(7) - C(6) - C(14)	121(1)	C(4B) - C(12C) - C(7A)	121.0(9)
C(6) - C(7) - C(7A)	121(1)	C(12B) - N(13) - C(13A)	119.6(8)
C(7) - C(7A) - N(8)	122(1)	C(12B) - N(13) - C(17)	120.0(8)
C(7) - C(7A) - C(12C)	118.8(9)	C(13A) - N(13) - C(17)	118.8(8)
N(8) - C(7A) - C(12C)	119.3(9)	N(13) - C(13A) - C(1)	121(1)
C(7A) - N(8) - C(8A)	123.5(9)	N(13) - C(13A) - C(4A)	120.7(9)
C(7A) - N(8) - C(15)	119.5(9)	C(1) - C(13A) - C(4A)	118(1)
C(8A) - N(8) - C(15)	116.7(9)	N(8) - C(15) - C(16)	108(1)
N(8) - C(8A) - C(9)	122(1)	N(13) - C(17) - C(18)	111.8(8)
N(8) - C(8A) - C(12A)	117.2(9)		

Table 3. Intermolecular distances shorter than 3.6\AA for C-C and C-N contacts and shorter than 4.0\AA for I⁻-C and I⁻-N contacts.

C(6) C(11 ¹)	3.57(2)	I(1) C(19)	3.76(1)
C(7) C(11 ¹)	3.55(2)	I(1) C(20A ¹¹)	3.68(1)
C(10) C(4B ¹)	3.38(2)	I(1) C(20B ¹¹)	3.67(1)
C(12) C(7A ¹)	3.39(2)		
C(11) C(7A ¹)	3.55(2)		

 symmetry codes: 1 3-x 1-y 2-z ii 2-x -y 1-z

A scheme of the overlap is shown in Fig. 5. The closest contacts between the two overlapping units are between C(7A),....C(12) and C(4B)....C(10) (Table 3).

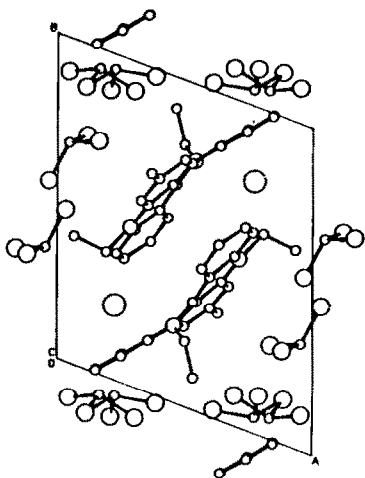


Fig. 4. Projection along c axis showing molecular packing.

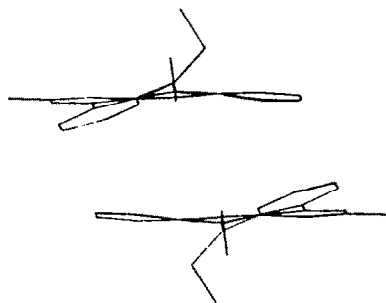


Fig. 5. Scheme of the cation overlapping.

EXPERIMENTAL

Synthesis

Piperidine (1 ml, 0.01 mole) was added to a boiling solution of N-ethyl-quinaldinium iodide (3 g, 0.01 mole) in ethanol (100 ml), and the mixture was boiled for 10 hrs. After concentration to 20 ml and cooling to room temp., a red crystalline precipitate of 8,13-diethyl-6-methyl-8H-quino[4,3,2-de]acridinium iodide is obtained, m.p. 204 - 205 °C after recrystallization from acetone (1.47 g, 63.2%).

The product is easily soluble in trifluoroacetic acid and trifluoroacetone, and slightly soluble in methanol, ethanol, acetone, chloroform, methylene chloride, nitromethane, DMF and DMSO.

TLC: Silicagel (Merck, 0.25 mm), eluent: n-butanol - acetic acid - water (1:1:2), $R_f = 0.36$.

Elemental analysis: 61.13% C, 5.29% H, 6.34% N; $C_{24}H_{23}N_2I$ requires: 61.81% C, 4.97% H, 6.01% N.

Spectra:

NMR spectra were measured at room temperature as solutions in DMSO- d_6 to provide the deuterium lock, with internal TMS as reference.

The 1H NMR spectrum was recorded at 100 MHz on Varian XL 100 spectrometer. The ^{13}C NMR spectra were recorded on a Jeol Co FX 90Q 22.50 MHz spectrometer. 8000 scans were accumulated for the proton decoupled ^{13}C spectrum and 20000 scans for the ^{13}C spectrum with off-resonance proton spin decoupling. A 7 μs pulse width with a repetition time of 1.1 s, a spectral width of 4000 Hz and 8K data points were utilized for accumulation, which were then Fourier transformed with a Jeol-980 computer.

¹H NMR:

δ (ppm)	multiplicity	No of protons	assignment
1.22	t	3	} N-ethyl groups
1.72	t	3	
4.83	q	2	
5.31	q	2	
2.85	s	3	methyl group at aromatic ring
7.63-8.55	multiplet	10	protons of aromatic rings.

¹³C NMR: δ (ppm), assignment

aliphatic carbon atoms:

11.76, 15.17 - CH₃ of N-ethyl groups42.60, 52.06 - CH₂ of N-ethyl groups22.17 - CH₃ group at aromatic ring

aromatic carbon atoms:

114.99, 115.21, 123.12, 130.98, 136.23, 138.79, 141.82, 148.15, 152.75 - quaternary carbon atoms of heteroaromatic ring;

112.82, 115.73, 117.07, 120.67, 122.70, 126.27, 124.53, 129.23, 130.73, 135.84 - other carbon atoms of heteroaromatic ring.

X-ray structure determination:

Red crystals were obtained by recrystallization from chloroform. X-ray diffraction data were collected on a Syntex P2₁ diffractometer from a well - formed crystal with dimensions 0.5 × 0.4 × 0.4 mm. The crystals of [C₂₄H₂₃N₂]⁺ I⁻ 2 CHCl₃ are triclinic, P1, with a = 11.858(4), b = 13.120(4), c = 11.091(2) Å, α = 94.46(2), β = 113.84(2), γ = 106.48(2)^o, V = 1476.6(6) Å³, Z = 2, μ(Mo Kα) = 15.23 cm⁻¹, D_m = 1.57, D_x = 1.59 gcm⁻³. 3585 unique reflections with 2θ ≤ 45^o were measured of which 2503 had I ≥ 1.96 σ(I) and were considered observed. The I⁻ ion position was found from a Patterson map and the positions of the remaining atoms were determined using the DIRDIF³ program. The structure was refined by full-matrix least-squares techniques (with counter-weights) to a final value of R = 0.058 and R_w = 0.055. The final refinement included anisotropic non-H atoms and an empirical isotropic extinction parameter x, used to correct the calculated structure factors according to F_c' = F_c(1 - xF_c² / sinθ), which converged at x = 1.9(2) 10⁻³. All hydrogen atoms were placed in idealized positions and contributed to F_c but were not refined. All calculations were performed using DIRDIF³, SHELX 76⁴ and local programs⁵. ORTEP⁶ and PLUTO⁷ were used for drawings. All supplementary crystallographic data are available on request from the Cambridge Crystallographic Data Centre⁸.

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