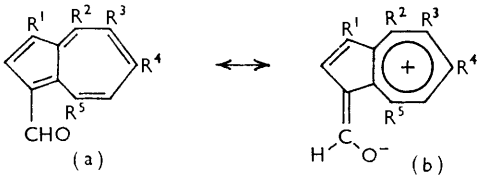
30. *Conjugated Cyclic Hydrocarbons and Their Heterocyclic Analogues. Part IV.*[1] *Dimethinecyanine Salts from 1-Formylazulenes and Heterocyclic Quaternary Ammonium Salts.*

By E. C. Kirby and D. H. Reid.

1-Formylazulenes (I—IV) condense with reactive heterocyclic quaternary ammonium salts in the presence of bases to give dimethinecyanine salts (V). The relation of this novel class of dye to known classes of cyanine salt is noted. Light absorption data for the salts are recorded.

Previous studies have shown that 1-formylazulenes (I—IV) show differences in behaviour from benzenoid aromatic aldehydes. The reduced electrophilic character of the carbonyl group is correlated with greater polarisability in the azulenes which are best represented in the ground state as resonance hybrids to which the dipolar forms (Ib—IVb) make important contributions.



(I) : $R^1 = R^2 = R^3 = R^4 = R^5 = H$
(II) : $R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = H$
(III) : $R^1 = R^5 = Me$, $R^2 = R^4 = H$, $R^3 = Pr^i$
(IV) : $R^1 = R^3 = H$, $R^2 = R^4 = R^5 = Me$

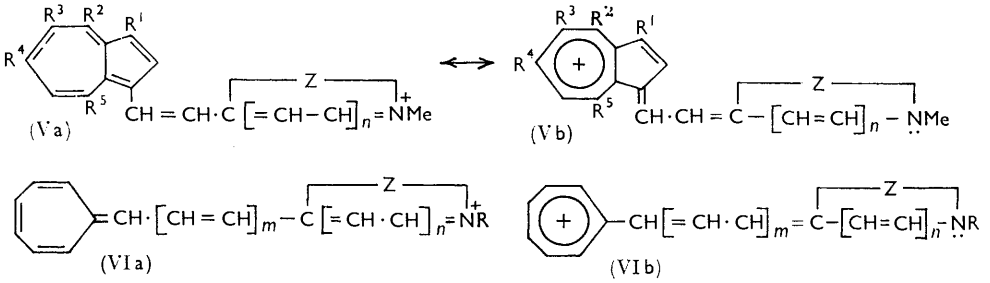
This formulation accounts satisfactorily for (i) the failure of 1-formylazulenes to undergo the Cannizzaro reaction, the benzoin condensation, and oxidation to the corresponding carboxylic acids,[2] and (ii) the formation of stable hydroxymethyleneazulenium salts on treatment of 1-formylazulenes with strong acids.[3]

Alkylation increases the importance of the dipolar structures (Ib—IVb) to the resonance hybrid by inductive and hyperconjugative stabilisation, and increases thereby also the abnormality in behaviour of the aldehyde. Thus 3-formylguaiazulene (1-formyl-5-isopropyl-3,8-dimethylazulene) (III), unlike 1-formylazulene[2] (I), fails to react with

[1] Part III, *J.*, 1960, 663.
[2] Hafner and Bernhard, *Annalen*, 1959, **625**, 108.
[3] Kirby and Reid, *J.*, 1960, 494.

Grignard reagents,[4] behaves abnormally with lithium aluminium hydride,[4] and fails to condense with azulenes in the presence of 70% perchloric acid.[3] The position of alkylation influences the reactivity of the carbonyl group significantly for 1-formyl-4,6,8-trimethylazulene (IV) behaves like 1-formylazulene in these reactions.[2]

It has recently been shown [2] that 1-formyl-4,6,8-trimethylazulene condenses in the presence of bases with cyclopentadiene, nitromethane, diethyl malonate, and acetophenone. We now report that 1-formylazulenes condense in the presence of organic bases with



heterocyclic quaternary ammonium salts containing a reactive methyl group to form members of a novel class of dimethinecyanine salts (V) ($n = 0$ or 1; Z is the residue of

TABLE 1. *Visible absorption maxima of dimethinecyanine salts* (V) *in methanol.*

No.	Cation	X	λ (mμ) max.	log ε
1	3-[2-(Azulen-1-yl)vinyl]-2-methylisoquinolinium	ClO_4	446 *	4·53
2	2-[2-(Azulen-1-yl)vinyl]-1-methylpyridinium	ClO_4	469 *	4·64
3	2-[2-(Azulen-1-yl)vinyl]-1-methylpyridinium	I	469 *	4·63
4	2-[2-(Azulen-1-yl)vinyl]-3,4-dimethylthiazolium	I	481 *	4·58
5	2-[2-(Azulen-1-yl)vinyl]-3-methylthiazolium	ClO_4	481	4·64
6	4-[2-(Azulen-1-yl)vinyl]-1-methylpyridinium	I	482	4·69
7	2-[2-(Azulen-1-yl)vinyl]-3-methylbenzoxazolium	ClO_4	491	4·79
8	1-[2-(Azulen-1-yl)vinyl]-2-methylisoquinolinium	ClO_4	493 *	4·28
9	2-[2-(Azulen-1-yl)vinyl]-3-methylbenzothiazolium	ClO_4	514	4·78
10	2-[2-(Azulen-1-yl)vinyl]-1-methylquinolinium	ClO_4	522	4·79
11	4-[2-(Azulen-1-yl)vinyl]-1-methylquinolinium	I	541 *	4·70
12	2-Methyl-3-[2-(3-methylazulen-1-yl)vinyl]isoquinolinium	ClO_4	462	4·54
13	1-Methyl-2-[2-(3-methylazulen-1-yl)vinyl]pyridinium	ClO_4	489 *	4·65
14	3,4-Dimethyl-2-[2-(3-methylazulen-1-yl)vinyl]thiazolium	ClO_4	500 *	4·59
15	3-Methyl-2-[2-(3-methylazulen-1-yl)vinyl]thiazolium	ClO_4	502 *	4·61
16	1-Methyl-4-[2-(3-methylazulen-1-yl)vinyl]pyridinium	ClO_4	502 *	4·71
17	3-Methyl-2-[2-(3-methylazulen-1-yl)vinyl]benzoxazolium	ClO_4	509	4·79
18	3-Methyl-2-[2-(3-methylazulen-1-yl)vinyl]benzothiazolium	ClO_4	533	4·80
19	1-Methyl-2-[2-(3-methylazulen-1-yl)vinyl]quinolinium	ClO_4	543	4·80
20	1-Methyl-4-[2-(3-methylazulen-1-yl)vinyl]quinolinium	I	563	4·71
21	2-[2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl]-1-methylpyridinium	ClO_4	509 *	4·65
22	4-[2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl]-1-methylpyridinium	I	524 *	4·72
23	2-[2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl]-3-methylthiazolium	ClO_4	525 *	4·69
24	2-[2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl]-3-methylbenzothiazolium	ClO_4	550 *	4·78
25	4-[2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl]-1-methylquinolinium	I	592 *	4·72
26	1-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]pyridinium	ClO_4	482 *	4·59
27	1-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]pyridinium	I	482 *	4·59
28	3-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]benzoxazolium	ClO_4	497	4·76
29	3,4-Dimethyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]thiazolium	ClO_4	499 *	4·61
30	3,4-Dimethyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]thiazolium	I	499 *	4·59
31	3-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]thiazolium	ClO_4	499	4·61
32	1-Methyl-4-[2-(4,6,8-trimethylazulen-1-yl)vinyl]pyridinium	ClO_4	499	4·64
33	1-Methyl-4-[2-(4,6,8-trimethylazulen-1-yl)vinyl]pyridinium	I	499	4·64
34	3-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]benzothiazolium	ClO_4	530 *	4·74
35	1-Methyl-2-[2-(4,6,8-trimethylazulen-1-yl)vinyl]quinolinium	ClO_4	567	4·22
36	1-Methyl-4-[2-(4,6,8-trimethylazulen-1-yl)vinyl]quinolinium	I	572 *	4·63

* Centre of very broad maximum.

[4] Reid, Stafford, and Stafford, *J.*, 1958, 1118.

a heterocyclic nucleus). The methyl group in the heterocycle is situated so that resonance occurs in the product between structures (Va) in which the positive charge is carried by quaternary nitrogen, and structures (Vb) in which the seven-membered ring has assumed the tropylium structure. The dimethinecyanine salts (V) are examples of one of several novel classes of cyanine dyes derived from the parent hypothetical structure (VI) [*n* and Z are as in (V), $m = 0, 1, 2$, etc.]. Structurally they occupy a position between those cyanine dyes whose cationic resonance involves tertiary and quaternary nitrogen, and the all-carbon 1,1′-azulylmethyleneazulenium salts.[3]

Heterocycles whose quaternary salts reacted with 1-formylazulene to form salts (V $R^1 = R^2 = R^3 = R^4 = R^5 = H$) were 2- and 4-methyl-pyridine and -quinoline, 2-methylbenzoxazole and -benzothiazole, 2-methyl- and 2,4-dimethyl-thiazole, and 1- and 3-methylisoquinoline. Exceptionally, 2,3-dimethylisoquinolinium perchlorate reacted sluggishly,

TABLE 2. *Condensation of* 1-*formylazulenes* (I—IV) *with heterocyclic quaternary ammonium salts.*

Procedure	Heterocyclic quaternary ammonium salt	Product no.	Yield (%)	Colour †	M. p.‡
	(a) 1-*Formylazulene* (I)				
E [a]	2,3-Dimethylisoquinolinium perchlorate	1	44	Brown [b]	>340° * [c]
A	1,2-Dimethylpyridinium perchlorate	2	78	Reddish-brown	301—302·5 *
A	,, ,, iodide	3	32	Reddish-brown	271—273 *
A	2,3,4-Trimethylthiazolium iodide	4	55	Reddish-brown	266—267 *
A	2,3-Dimethylthiazolium perchlorate	5	62	Grey-blue [d]	257 *
A	1,4-Dimethylpyridinium iodide	6	56	Brown	>291 [e]
A	2,3-Dimethylbenzoxazolium perchlorate	7	36	Brown	>320 [e]
A	1,2-Dimethylisoquinolinium perchlorate	8	46	Brown	294—297 *
A	2,3-Dimethylbenzothiazolium perchlorate	9	66	Black	307—310 *
A	1,2-Dimethylquinolinium perchlorate	10	68	Reddish-purple	298·5—300 *
A	1,4-Dimethylquinolinium iodide	11	50	Green	269—271 *
	(b) 1-*Formyl*-3-*methylazulene* (II)				
E [a]	2,3-Dimethylisoquinolinium perchlorate	12	35	Brown	>324 *
B	1,2-Dimethylpyridinium perchlorate	13	44	Black	299—301 *
B	2,3,4-Trimethylthiazolium perchlorate	14	66	Black [g]	291—292·5 *
B	2,3-Dimethylthiazolium perchlorate	15	66	Bluish-black	264—265 *
B	1,4-Dimethylpyridinium perchlorate	16	54	Green	278 *
B	2,3-Dimethylbenzoxazolium perchlorate	17	80	Green [d,h]	302—305*
B	2,3-Dimethylbenzothiazolium perchlorate	18	66	Violet-black	* [j]
B	1,2-Dimethylquinolinium perchlorate	19	96	Green	322—323 *
B	1,4-Dimethylquinolinium iodide	20	70	Black [k]	284—289 *
	(c) 1-*Formyl*-5-*isopropyl*-3,8-*dimethylazulene* (III)				
E	1,2-Dimethylpyridinium perchlorate	21	60	Black [l,m]	>205 [n]
E	1,4-Dimethylpyridinium iodide	22	77	Black [d,g,o]	219—227 [p]
E	2,3-Dimethylthiazolium perchlorate	23	73	Green [m]	254—256 *
E	2,3-Dimethylbenzothiazolium perchlorate	24	48	Violet-black	>150 [n]
E	1,4-Dimethylquinolinium iodide	25	36	Black [q]	250—255 *
	(d) 1-*Formyl*-4,6,8-*trimethylazulene* (IV)				
E	1,2-Dimethylpyridinium perchlorate	26	43	Dark brown	264·5—271·5 * [p]
E	,, ,, iodide	27	42	Dark brown	257·5—259·5 * [p]
A	2,3-Dimethylbenzoxazolium perchlorate	28	3	Reddish-brown [q,r]	285—290 *
D	2,3,4-Trimethylthiazolium perchlorate	29	74	Dark green	296·5—301·5 * [p]
D	,, ,, iodide	30	74	Dark green	268—270 * [p]
C	2,3-Dimethylthiazolium perchlorate	31	56	Purple	270—274 * [p]
E	1,4-Dimethylpyridinium perchlorate	32	79	Dark green	271—274 * [p]
E	,, ,, iodide	33	75	Dark green	[ps]
C [t]	2,3-Dimethylbenzothiazolium perchlorate	34	59	Deep purple	276—277 [p]
C	1,2-Dimethylquinolinium perchlorate	35	63	Deep purple [u]	[pv]
C	1,4-Dimethylquinolinium iodide	36	43	Dark brown	[pw]

TABLE 2. (*Continued.*)

Product	Found (%)						Required (%)				
no.	C	H	Hal	N	S	Formula	C	H	Hal	N	S
1				3·7		$C_{22}H_{18}ClNO_4$				3·5	
2				4·5		$C_{18}H_{16}ClNO_4$				4·1	
3	58·0	4·6	33·7	3·8		$C_{18}H_{16}IN$	57·9	4·3	34·0	3·8	
4	52·6	4·2			8·0	$C_{17}H_{16}INS$	51·9	4·1			8·1
5			9·9	3·9	8·9	$C_{16}H_{14}ClNO_4S$			10·1	4·0	9·1
6	57·5	4·0	35·0	4·0		$C_{18}H_{16}IN$	57·9	4·3	34·0	3·8	
7	61·8	3·9	8·8	3·7		$C_{20}H_{16}ClNO_5$	62·4	4·2	9·2	3·6	
8				3·6		$C_{22}H_{18}ClNO_4$				3·5	
9	59·7	4·0	9·0	3·8	8·2	$C_{20}H_{16}ClNO_4S$	59·8	4·0	8·8	3·5	8·0
10	67·3	5·0		3·8		$C_{22}H_{18}ClNO_4$	66·8	4·6		3·5	
11	63·0	4·7		3·1		$C_{22}H_{18}IN$	62·4	4·3		3·3	
12	66·8	5·0		3·3		$C_{23}H_{20}ClNO_4$	67·4	4·9		3·4	
13	63·9	4·8	10·0	3·9		$C_{19}H_{18}ClNO_4$	63·4	5·0	9·9	4·0	
14			8·8	3·8		$C_{18}H_{18}ClNO_4S$			8·8	3·7	
15 [z]			8·9		7·9	$C_{17}H_{16}ClNO_4S$			9·7		8·8
16	63·3	5·0	9·5	3·9		$C_{19}H_{18}ClNO_4$	63·4	5·0	9·9	3·9	
17	63·5	4·5	9·1	3·6		$C_{21}H_{18}ClNO_5$	63·1	4·5	8·9	3·5	
18			8·9	3·5	8·0	$C_{21}H_{18}ClNO_4S$			8·5	3·4	7·7
19	67·5	5·1		2·9		$C_{23}H_{20}ClNO_4$	67·4	4·9		3·4	
20	63·0	4·9		3·3		$C_{23}H_{20}IN$	63·2	4·6		3·2	
21				3·1		$C_{23}H_{26}ClNO_4$				3·4	
22				3·1		$C_{23}H_{26}IN$				3·2	
23				3·1		$C_{21}H_{24}ClNO_4S$				3·3	
24				2·8		$C_{25}H_{26}ClNO_4S$				3·0	
25				3·1		$C_{27}H_{28}IN$				3·0	
26	65·0	5·7	9·7	3·8		$C_{21}H_{22}ClNO_4$	65·0	5·7	9·1	3·6	
27	60·8	5·5	31·1	3·6		$C_{21}H_{22}IN$	60·7	5·3	30·6	3·4	
28	64·9	5·3		3·3		$C_{23}H_{22}ClNO_5$	64·6	5·2		3·3	
29	59·9	5·8	8·2	3·2	7·6	$C_{20}H_{22}ClNO_4S$	58·9	5·4	8·7	3·4	7·9
30	55·5	5·1		3·1		$C_{20}H_{22}INS$	55·2	5·1		3·2	
31	57·9	5·1	9·1	3·6	8·0	$C_{19}H_{20}ClNO_4S$	57·9	5·1	9·0	3·6	8·1
32	65·2	5·7	9·1	3·8		$C_{21}H_{22}ClNO_4$	65·0	5·7	9·1	3·6	
33	60·5	5·2	30·8	3·5		$C_{21}H_{22}IN$	60·7	5·3	30·6	3·4	
34	62·6	5·2	7·7	3·2	7·2	$C_{23}H_{22}ClNO_4S$	62·2	5·0	8·0	3·2	7·2
35			8·2	3·1		$C_{25}H_{24}ClNO_4$			8·1	3·2	
36	64·6	5·4		3·2		$C_{25}H_{24}IN$	64·5	5·2		3·0	

* With decomp. † Needles unless otherwise stated. ‡ Heating stage preheated to *ca.* 10° below the m. p. unless otherwise stated.

[a] Boiled for 30 min. [b] Powder. [c] Partial melting with blackening. [d] Recryst. from acetonitrile–ethanol (1 : 2). [e] Decomp. without melting. [f] Above 315° colour change from brown through grey to black. [g] Green reflex. [h] Red reflex. [i] Softens >290°. [j] Melts on block preheated to <323°. [k] Prisms. [l] Plates. [m] Recryst. from MeOH. [n] Gradual melting to a tar. [o] Flat needles. [p] Placed on heating stage at room temperature. [q] Indefinite form. [r] Washed with hot water; recryst. from EtOH. [s] Does not melt < 340°. [t] Condensation in 50 ml. of ethanol; solution concentrated to 25 ml. before crystallisation. [u] Recryst. from acetonitrile–ethanol (1 : 4). [v] Softens >235°. [w] Softens >350°. [z] No satisfactory analysis.

a result in agreement with the known lower reactivity of the 3- than of 1-methylisoquinoline and their quaternary salts.[5]

Alkylation lowers, but does not repress completely, the carbonyl reactivity of 1-formylazulene. 1-Formyl-3-methylazulene (II) behaved like the parent (I), condensing with all the heterocyclic quaternary salts cited. However, products could not be isolated after treatment of 3-formylguaiazulene or 1-formyl-4,6,8-trimethylazulene with the weakly reactive 2,3-dimethylisoquinolinium perchlorate, or after that of 3-formylguaiazulene with 2,3-dimethylbenzoxazolium perchlorate. The violet-blue product from 3-formylguaiazulene and 1,2-dimethylquinolinium perchlorate was unstable; it could not be purified by recrystallisation.

The dimethinecyanine salts (V) crystallise well from acetonitrile, and in the solid state are stable to air and light. Their visible absorption spectra consists in all cases of a single, broad absorption band lacking fine structure. Table 1 records the position and intensity

[5] Mills and Smith, *J.*, 1922, 2724; Erlenmeyer, Baumann, and Sorkin, *Helv. Chim. Acta*, 1948, **31**, 1978; Brooker and White, *J. Amer. Chem. Soc.*, 1951, **73**, 1094.

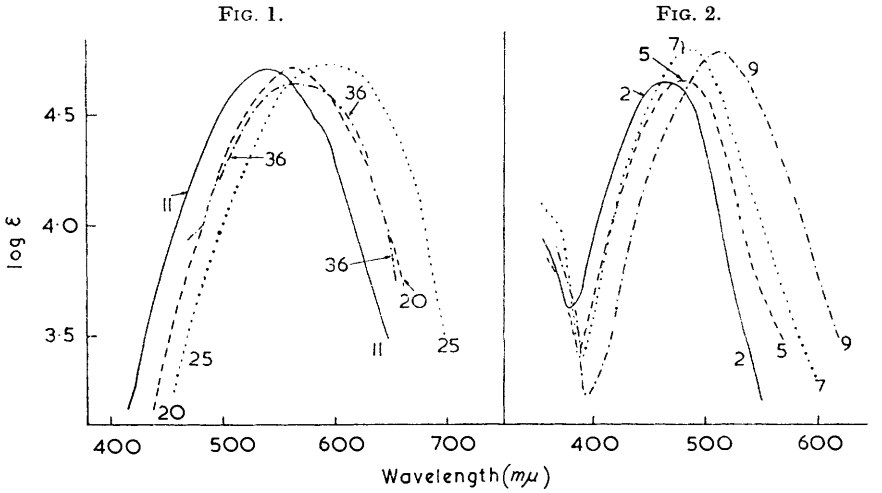
of this band for thirty-six salts. The following observations are noteworthy. (*a*) Alkylation of the azulene nucleus produces in all cases a bathochromic displacement of $\lambda_{max.}$ (Fig. 1). (i) A 3-methyl substituent produces an almost constant shift of +20 mμ (this drops to +16 mμ when the heterocyclic component is 3-isoquinoline). (ii) The same order of shift results from the combined effects of methyl substituents in the 4-, 6-, and 8-positions. (The shifts for compounds nos. 28, 35, and 36 of Table 1 deviate markedly from the mean value, being +6, +45, and +31 mμ, respectively.) (iii) Derivatives of guaiazulene show displacements of $\lambda_{max.}$ lying between +36 (compound no. 24) and +51 mμ (compound no. 25). (*b*) In each series with the same azulene nucleus, the absorption maximum shifts to longer wavelength as the heterocyclic component is changed in the order: 3-isoquinoline; 2-pyridine; 2-(4-methylthiazole), 2-thiazole, 4-pyridine; 2-benzoxazole; 1-isoquinoline; 2-benzothiazole; 2-quinoline; 4-quinoline [as an exceptional case, in the series derived from 1-formyl-4,6,8-trimethylazulene, compound no. 28 precedes compounds nos. 29—33 by a small decrement (2 mμ) in order of increasing wavelength] (see Fig. 2).

Experimental

M. p.s were determined on a Kofler-type heating stage. Visible spectra were determined with a Unicam S.P. 600 instrument. Specimens for analysis were dried for 4—6 hr. at 90°/0·1 mm. Acetonitrile was purified by successive distillations from phosphoric anhydride and freshly dried potassium carbonate

Condensation of 1-Formylazulenes with Heterocyclic Quaternary Ammonium Salts.—Condensations were by one of the following general procedures (for details see Table 2).

Procedure A. A mixture of the 1-formylazulene (0·003 mole), the heterocyclic quaternary ammonium salt (0·003 mole), piperidine (0·25 ml.), and ethanol (25 ml.) was boiled for 5 min. In most cases the product partly crystallised from the boiling solution. It was filtered off



Figs. 1 and 2.—*Absorption spectra for methanol solutions of dimethinecyanine salts* (V) (*numbers refer to Table* 1).

from the cooled solution, washed with a small volume of ethanol, and, unless otherwise stated, recrystallised from acetonitrile.

Procedures B, C, D, and E. These were identical with procedure A except that the quantity of piperidine used was, respectively, 0·4, 0·5, 1 and 2 ml.

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