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Synthesis and Evaluation of Retinal Schiff Base Salts and Related Compounds as Radar Absorbing Agents

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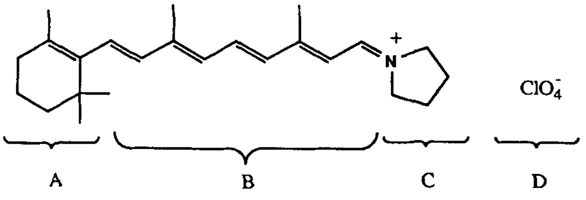
Abstract. Thirteen Schiff base salts in the class of compounds represented by retinal pyrrolidinium perchlorate were prepared (most of them for the first time), fully characterized analytically and spectroscopically, and examined in the 30 – 100 GH$_z$ range with respect to their putative ability to absorb radar signals. While some signal loss was noted with salts having I_3^- counterions, the compounds of this class show negligible potential as components of radar-absorbing coating systems.

1 Introduction

Stealth [1] is an amalgam of several technologies, one of which seeks to minimize the reflectance of military objects in the radio-frequency range of radiation. The diminution of reflected signal strength, commonly referred to as "loss", can be accomplished through scatter, destructive interference, or intrinsic absorption. While coating systems relying on the first two mechanisms have been developed, suitable materials with intrinsic energy absorbing properties in the 30 – 100 gigahertz (radar) region have yet to be identified.

In early 1987, an article appeared in an aviation trade publication announcing the discovery of radar absorbing properties in retinal Schiff base salts [2].



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This report stated that these materials would be capable of reducing aircraft radar reflectance by 80%. While the original report was not substantiated, an expanded version of it subsequently appeared in the New York Times, complete with a mechanistic rationale based on translational motion of the (perchlorate) counterion along the polyene backbone [3]. References to this phenomenon continue to appear in the press [4].

Retinal iminium salts have been the subject of long and intensive study because of their relevance to vision [5], but for this same reason most studies address their electronic absorption properties. Having both ready access to a variety of vitamin A-related chemicals (at Roche) and facilities for measuring radio-frequency absorption characteristics (at Boeing), we undertook the synthesis and evaluation as radar absorbers of a representative cross-section of compounds in this class.

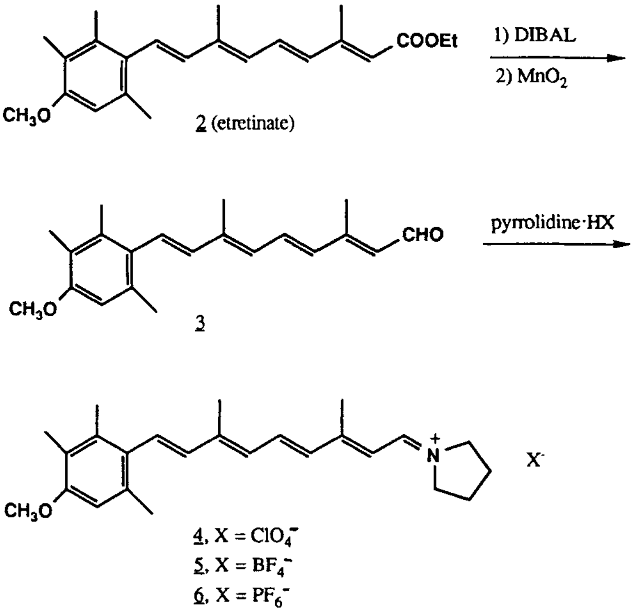
Compound **1**, on which the original report was based, can be regarded as the prototype of the class and our first task entailed the preparation of kilogram quantities for thorough evaluation. Our plan was then to use absorption data from **1** as a baseline and determine in a somewhat systematic manner the effects of structural changes in the segment labeled A through D.

2 Preparation of Materials

The availability of etretinate (**2**), a commercial antipsoriatic agent, facilitated the replacement of segment A in structure **1** with an aromatic moiety (Scheme 1).

Significant extension of the polyene chain segment B was achieved by preparing the Schiff base salts **8, 9** and **10** from β-apo-carotenal (**7**) (Scheme 2).

Attempts to probe the effect of further extending the polyene chain segment were carried out using torularhodinaldehyde (**11**) [6][1] as the Schiff base precursors without success. No characterizable salts could be obtained.

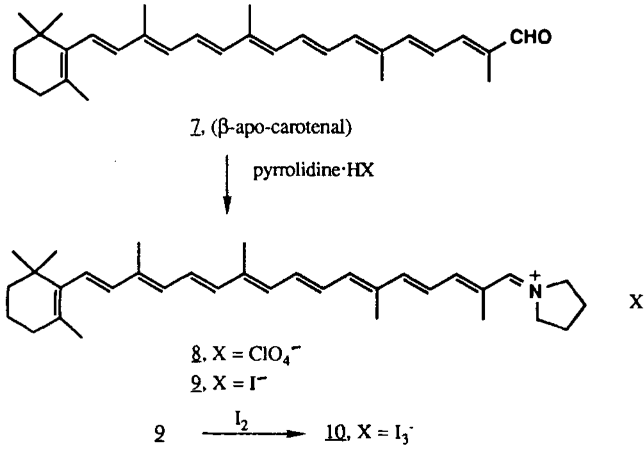


2 (etretinate)

3

4, $X = ClO_4^-$
5, $X = BF_4^-$
6, $X = PF_6^-$

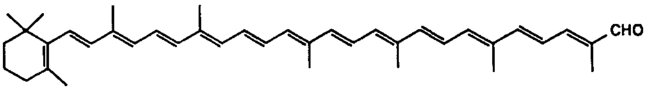
Scheme 1



7, (β-apo-carotenal)

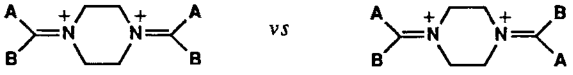
8, $X = ClO_4^-$
9, $X = I^-$
10, $X = I_3^-$

Scheme 2

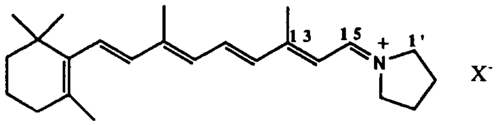


11 (torularhodinaldehyde)

Structural change in segment C, the secondary amine used to prepare the Schiff base salts, was considered with lower priority. The one change contemplated could not be effected. This entailed the substitution of piperazine for pyrrolidine and the preparation of a dimeric retinal-derived salt with an anticipated "double oscillator" effect. However, the piper-azine-based system is complicated by the cis/trans dichotomy depicted and no characterizable salts of this type could be obtained.



The most significant effects on signal loss were expected from variations in the counterion, segment D in structure **1**. This expectation arose from the attribution of signal loss to energy absorption associated with translational motion of the counterion along the polyene backbone [2] and the prediction that heavier anions would enhance the effect [7][2]. We accordingly prepared the series of salts **12 – 17**.



12, $X = Cl^-$
13, $X = Br^-$
14, $X = BF_4^-$
15, $X = PF_6^-$
16, $X = I^-$
17, $X = I_3^-$

The chloride and bromide were prepared using metathetical reactions of perchlorate **1** with the rubidium halides, advantage being taken of the low solubility of rubidium perchlorate in methanol. Salts **14** through **16** were prepared directly from the corresponding pyrrolidine/acid salts. The triiodide **17**, the salt with the heaviest anion studied, was prepared from the iodide **16** and iodine in methylene chloride. Compounds **10** and **17** are among the few well-characterized iminium triiodides known to date.

The NMR chemical shifts of H-15, H-1′ and CH_3-13 vary significantly with the change in the counterion. A trend can be clearly observed by focusing on the retinal derivatives **12, 13, 16** and **17**. The change in

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[1] We are grateful to Dr. Urs Hengartner, Roche Basel, for a supply of torularhodinaldehyde.

[2] Private communication with Professor R. R. Birge, Syracuse University.

chemical shifts is attributed to a combination of the change in electronegativity and radius of the counterion. A decrease in chemical shift is observed with a decrease in electronegativity and an increase in radius of the counterion down the halogen group. Thus, a tighter ion pair is formed with a smaller more electronegative counterion. The strongest bond is in the case of the chloride (**12**).

An examination of the relative change in chemical shift with change of counterion for each of the protons of the polyene chain reveals that I_3^-, relative to the other anions, deshields significantly the protons, H-7, H-8, H-10, and H-11, farthest along the polyene chain. Thus, the largest downfield shifts of these protons are observed in the case of the I_3^- salt, shifts attributable to the great length of an I_3^- anion.

The UV-vis spectra were recorded in ethanol or in methanol and in some cases, also in chloroform (compound **14** is not soluble in ethanol, spectrum measured in chloroform only). As expected [6] the main maximum of the all-trans-retinyl pyrrolidinium salts (compounds **1, 12, 13, 14, 15, 16**) in ethanol or in methanol is in the 450 – 455 nm range. In a polarizable nonpolar solvent such as chloroform, it is shifted to about 480 nm probably due to a substantial induced dipole interaction.

The compounds (**4, 5** and **6**) containing an aromatic ring instead of a cyclohexene ring exhibit long wavelength maxima also in the 450 – 455 nm area in ethanol. As predicted, the main absorption maximum of the β-apocarotenal pyrrolidinium salts (compounds **8** and **9**) is shifted to about 539 nm due to the additional conjugated ethylene moieties. The triiodide salts show additional maxima caused by the absorption of this anion. In two or three cases, the absorption spectra indicated the presence of more than one isomer.

Discussion of Microwave Absorption

Values for the real and imaginary components of the complex relative permittivity (also known as the frequency dependent dielectric constant) are given in Table 3 for the Schiff base salt/polymer systems at several frequencies between 30 and 100 GH_z.

Values are also given for a pure polymer sample and 2 % and 10 % (by weight) carbon-loaded silicone rubber samples[3] (Cabot Corporation Vulcan XC-72 carbon black in Dow Corning Sylgard 184). None of the salts exhibited magnetic behavior and as such permeability was not measured. For the salt/polymer matrix systems the real component of the permittivity hovers around the value 3, while the imaginary component consistently remains less than 0.10. These values, which are typical for nonconductive materials, indicate little interaction between the sample and electromagnetic radiation in the microwave region. That is, the salt/polymer samples were basically transparent at microwave frequencies.

Lack of activity at microwave frequencies is further demonstrated by comparing the permittivities of the salt/polymer mixtures to those for the neat polymer and the carbon black samples. It is observed that permittivity values for the salt/polymer samples are very similar to those for the neat polymer, which indicates that the salts have little impact on the inherent activity of the polymer. Comparison to the carbon-loaded samples shows that carbon black at low loadings yields permittivities which consistently exceed those for the much higher loaded Schiff base salt samples. This is especially evident for the imaginary component (i. e., the lossy component). The imaginary components for the 2 % carbon-loaded samples are typically an order of magnitude larger than similar values for the Schiff base salt samples. For the 10 % carbon-loaded samples, it is an order of magnitude larger again. The relationship between permittivity, complex index of refraction and absorption of electromagnetic radiation is discussed extensively elsewhere [7]. From the values presented here, the conclusion is that the Schiff base salts are relatively inactive in the 30 – 100 GH_z frequency range, and they are not radar absorbers.

The support of Dr. Wallace Smith through the office of Naval Research Contract No. N000014-89-C-0176 is gratefully acknowledged. We are also indebted to Mr. M. Lanyi, Mrs. N. Ciolko, Mrs. S. Rodgers, and Mrs. P. Tedesco for their skillful technical assistance.

Experimental

1 Materials

The spectral quality solvents, chloroform, ethanol, and methanol, were purchased from Fisher Scientific Co., Fair Lawn, New Jersey, and were used without further purification and $CDCl_3$ and DMSO-d_6 were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin.

2 Spectroscopic Measurements

Melting points are uncorrected. All compounds were characterized by NMR, UV-Vis, IR and MS spectral measurements and elemental analysis. In each case, the analytical results were found to be in agreement with the structure.

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian XL-400 FT-NMR spectrometer. The chemical shifts are summarized in Table 1. The UV-Vis spectra were measured in ethanol, methanol and/or in chloroform on

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[3] The authors wish to thank William Injerd for providing the carbon black data.

Table 1 ^{1}H and ^{13}C NMR Data[a]

Compound	H-7	H-8 H-8′	H-10 H-10′	H-11 H-11′	H-12 H-12′	H-14 H-14′	H-15 H-15′	H-1′	H-2′	H-3′	H-4′	CH_3-9 CH_3-9′	CH_3-13 CH_3-13′
1	6.51	6.24	6.27	7.42	6.59	6.32	8.81	4.20	2.12	2.20	3.87	2.09	2.38
12	6.51	6.23	6.28[c]	7.42	6.56	6.26[c]	9.96	4.48	2.12	2.21	3.87	2.09	2.56
13	6.53	6.23	6.26[c]	7.44	6.55	6.24[c]	9.71	4.47	2.14	2.21	3.84	2.10	2.56
14	6.50	6.23	6.27	7.41	6.60	6.33	8.79	4.15	2.08	2.19	3.86	2.06	2.36
15	6.53	6.24	6.24	7.43	6.55	6.27	8.63	4.13	2.12	2.20	3.82	2.09	2.36
16	6.53	6.24	6.27	7.44	6.57	6.27	9.45	4.43	2.16	2.20	3.83	2.10	2.53
17	6.57	6.28	6.34	7.52	6.65	6.34	8.75	4.24	2.25	2.31	3.95	2.12	2.49
4	6.93	6.33	6.24	7.47	6.56	6.31	8.90	4.23	2.15	2.20	3.85	2.32	2.44
5	6.94	6.33	6.30	7.47	6.55	6.21	8.90	4.23	2.15	2.21	3.82	2.32	2.43
8	6.23	6.15	6.17	6.79	6.37	6.30	6.91	4.20	2.08	2.23	4.16	2.04	2.00
		8.41	7.51	6.60	7.06	6.65	6.65					2.24	1.97
9	6.23	6.15	6.17	6.79	6.37	6.29	6.92	4.40	2.10	2.22	4.13	2.05	2.00
		9.29	7.86	6.60	7.13	6.64[c]	6.66[c]					2.24	1.98
10	6.24	6.14	6.17	6.81	6.37	6.31	6.97	4.25	2.19	2.30	4.22	2.04	2.02
		8.39	7.66	6.78	7.23	6.64	6.69					2.31	2.00

Compound	C-7	C-8 C-8′	C-9 C-9′	C-10 C-10′	C-11 C-11′	C-12 C-12′	C-13 C-13′	C-14 C-14′	C-15 C-15′	C-1′	C-2′	C-3′	C-4′	CH_3-9 CH_3-9′	CH_3-13 CH_313′
14	132.49	136.73	137.56	129.75	138.78	134.07	166.20	118.42	160.02	56.83	24.47[c]	24.61[c]	50.83	13.26	14.18
15	132.86	136.29	137.56	129.64	139.29	133.75	166.65	117.96	159.64	56.84	24.46[c]	24.60[c]	50.70	13.30	14.19
17[b]	130.89	136.49	137.12	129.91	138.10	133.96	164.00	119.09	160.11	56.28	23.98	23.98	50.65	12.94	14.09
4[b]	132.40	137.43	145.13	129.81	138.94	134.20	156.72	118.45	160.42	57.05	24.53[c]	24.65[c]	50.92	13.40	14.49
5	132.45	137.52	146.36	130.25	138.90	134.22	156.68	118.28	160.37	56.95	24.50[c]	24.65[c]	50.74	13.36	14.35
9	127.78	137.57[c]	137.86[c]	130.63	127.52	136.56	141.27	130.63	131.88	59.06	23.55	25.87	52.49	13.13	13.77
		161.65	124.83	154.50	121.83	143.40	135.15	136.65	128.93					12.56[c]	12.88[c]

[a] Chemical shifts are in ppm downfield from TMS.

[b] Data were obtained in DMSO-d_6.

[c] Chemical shifts interchangeable between pairs of assignments.

Table 2 UV-Vis absorption spectral data

Compound	Solvent	μ max[a], nm (ε, M^{-1}, $cm^{-1} \times 10^{-3}$)			
1	Ethanol	237 (8.85)	267 (10.62)	453 (42.35)	
	Methanol	238 (8.45)	267 (9.75)	453 (45.35)	
	Chloroform	274 (10.75)	345 (8.26)	480 (41.80)	
4	Ethanol[b][c]	253 (10.80)	270 (sh) (10.39)	395 (29.34)	435 (i) (27.25)
5	Ethanol[c]	272 (13.47)	350 (i) (12.75)	453 (32.25)	
6	Ethanol[c]	273 (12.05)	350 (i) (13.23)	453 (35.00)	
8	Methanol	285 (sh) (10.15)	332 (19.65)	539 (64.12)	
9	Ethanol[b]	269 (14.15)	315 (9.22)	466 (72.35)[d]	580 (i) (17.22)
10	Chloroform[e]	281 (67.99)	360 (58.29)	598 (81.72)	
12	Ethanol[b][c]	252 (8.75)	340 (i) (10.84)	447 (21.40)[d]	
	Chloroform	272 (8.76)	239 (sh) (8.21)	461 (25.22)	
13	Ethanol	257 (9.67)	375 (i) (17.27)	445 (28.61)[d]	
14	Chloroform[e]	273 (10.92)	345 (8.51)	475 (41.60)	
15	Ethanol	264 (10.08)	350 (i) (13.00)	452 (40.77)	
16	Methanol	267 (10.65)	330 (sh) (18.43)	453 (44.25)	
17	Ethanol	291 (25.00)	375 (30.05)	447 (32.65)	

[a] (i) = inflection, (sh) = shoulder [b] mixture of isomers [c] absorption intensity lower than expected [d] maximum broad [e] not soluble in ethanol

a Cary recording spectrophotometer, Model 17D. The electronic absorption data is shown in Table 2. The IR spectra were recorded in chloroform (also few in diffuse reflectance mode) on a Digilab FTS-15E, FT-IR spectrophotometer. The MS spectra were obtained on a VG mass spectrometer, Model 7070E-HF. The elemental analysis were performed on a Liebman Laboratories automated CHN-analyzer, Model 440 CN. Microwave measurements were with a Hewlett-Packard network analyzer.

3 Loss Measurements

a) Instrumentation

Complex permittivity and permeability in the microwave and millimeterwave spectrum were determined by measuring the two-part complex scattering coefficients with a network analyzer [8]. In the 8 – 18 GH_z frequency range a waveguide-bridge configuration was used, while in the 26 to 40 GH_z and 75 to 100 GH_z ranges free-space techniques were used.

Procedures and analyses are the same for both configurations. Permittivity and permeability are related to the measured scattering coefficients by wellknown scattering equations [9].

b) Sample Preparation

Samples for measurements in the microwave region were prepared by dispersing the Schiff base salts in a polymer matrix. Weighed amounts of the salts were dispersed in a polyurethane resin system (Conap Incorporated Conathane EN-20), cast into flat sheets (approximately 15 × 15 × .25 cm) and allowed to cure. This process provided dimensionally stable samples which could be easily handled. Relative proportions of salt and polymer are given in Table 3. For waveguide measurements pieces were cut out of the sheets which fit inside the waveguide. Free-space measurements were made on the sheets supported in frames to keep them rigid. Some waveguide measurements were made on the pure salts in powder form, but these were unreliable as the density could not be controlled. Attempts were also made to make measurements on the salts dissolved in solvents such as dimethyl formamide, but the large permittivities of solvent masked any contribution from the salt.

(all trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium Perchlorate (**1**)[4)][5)]

A 12 l three-necked flask equipped with a mechanical stirrer, a thermometer, two addition funnels and a gas adapter was charged under an atmosphere of argon with 500 ml of 2B ethanol. The flask was cooled to 0 – 5 °C in an ice-bath and 430 ml (5.0 mol) of 70 % perchloric acid was added dropwise keeping the temperature below 7 ° throughout the addition of about 1.5 hr. The other addition funnel was charged with a solution of 418.5 ml (5.0 mol) of pyrrolidine in 875 ml of 2B ethanol. This solution was then added dropwise over a period of 4.5 hr to the perchloric acid solution keeping the temperature below 7 °C during the addition. When the addition of the pyrrolidine solution was complete, a solution of 5.0 kg of crude (30 – 40 %) vitamin A aldehyde (plant process stream) in 2.5 l of 2B ethanol was added over a period of 30 min. The reaction mixture was then allowed to reach room temperature and was stirred under an atmosphere of argon overnight. A solid precipitate formed. The mixture was then transferred into a large extractor containing 26.0 l of tetrahydrofuran, agitated for 5 – 10 min., and filtered under vacuum. The solids were washed with 4.0 l of tetrahydrofuran and air-dried overnight. The solids were then divided in two equal portions and transferred into two 22 l three-necked, round-bottomed flasks fitted with distillation condensers. Each flask was charged with 6.0 l of methylene chloride and the mixtures were heated to reflux to dissolve the solids. Each flask was further charged with 10.0 l of 2B ethanol and heating was continued until all of the methylene chloride was removed by distillation. The mixtures were then allowed to cool slowly to room temperature and stirred overnight to effect crystallization. The crystals were filtered under vacuum, air-dried for 2 hr and finally dried at 25 °/100 mm overnight to afford 1.02 kg of

Table 3 Complex permittivities at selected Frequencies[a)]

		Frequency (GH_z)									
		30		40		80		90		100	
Compound	Concentration[b)] (%)	ε′	ε″	ε′	ε″	ε′	ε″	ε′	ε″	ε′	ε″
1	50	3.40	0.066	3.29	0.023	3.47	0.092	3.40	0.085	3.28	0.070
15	62	3.39	0.020	3.33	0.034	3.43	0.042	3.42	0.043	3.31	0.052
17	57	2.94	0.020	2.92	0.028	2.95	0.055	2.94	0.060	2.85	0.093
8	37	3.08	0.009	3.07	0.011	3.14	0.093	3.10	0.075	3.01	0.078
5	30	2.76	0.021	2.75	0.026	2.76	0.083	2.74	0.022	2.72	0.059
4	54	3.22	0.041	3.17	0.016	3.23	0.078	3.20	0.080	3.10	0.075
Carbon Black	2	3.74	0.233	3.63	0.233	3.38	0.292	3.42	0.295	3.32	0.314
Carbon Black	10	8.21	1.32	7.77	1.30	7.05	1.54	6.92	1.57	6.78	1.49
EN-20[c)]	–	2.70	0.041	2.70	0.026	2.69	0.042	2.66	0.040	2.67	0.030

[a)] Permittivity $\varepsilon = \varepsilon' + i\varepsilon''$, where ε' is the real part and ε'' the imaginary part. Uncertainties in measured values are approximately 10 %.

[b)] Based on the weights.

[c)] Polyurethane resin system.

[4)] Scale-up and development of this procedure was carried out by Dr. Panos Kalaritis and Mr. Ronald Regenye.

[5)] The perchlorate salts and reaction mixtures containing perchloric acid described herein should be handled as potentially explosive materials. Avoid overheating!

product as a lustrous purple-black solid. The filtrates were concentrated to half volume by atmospheric distillation, and stirred at room temperature overnight to give a second crop. Filtration and drying then yielded an additional 233.0 g of product. The 1.25 kg of first and second crops were combined, m.p. 200 °C (dec) (Lit. [10] m.p. 194 – 195 °C). This material was >95 % all-**trans** based upon the ^{1}H NMR spectrum. Spectroscopic data is tabulated in Table 1.
Analysis: Calcd. C 65.81; H 8.28; N 3.20. Found: C 65.70; H 8.18; N 3.17

(all trans)-1-[9-(4-Methoxy-2,3,6-trimethylphenyl)3,7-dimethyl-2,4,6,8-nonnonatetraenylidene]pyrrolidinium perchlorate (**4**)

To a stirred suspension of 4 Å molecular sieves (15 g) and pyrrolidinium perchlorate [11] (40 g, 0.25 mol) in absolute ethanol (250 ml) under an argon atmosphere was added slowly a solution of aldehyde **3** (48.5 g, 0.156 mol) in methylene chloride (400 ml) at 0 °C. The reaction mixture was stirred for 48 h at room temperature, and then added to methylene chloride (500 ml). The whole mixture was filtered, the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (450 ml), the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 38.36 g (53 %) of the perchlorate salt **4** as red-brown crystals, m.p. 195.5 – 197.0 °C (dec).
Analysis: Calcd. C 64.71; H 7.39; N 3.02. Found: C 64.43; H 7.40; N 2.92.

(all-trans)-1-[9-(4-Methoxy-2,3,6-trimethylphenyl)-3,7-dimethyl-2,4,6,8-nonatetraenylidene]pyrrolidinium tetrafluoroborate (**5**)

To a stirred suspension of 4 Å molecular sieves (25 g) and pyrrolidinium tetrafluoroborate (32 g, 0.20 mol) in absolute ethanol (200 ml) under an argon atmosphere was added slowly a solution of aldehyde **3** (41.7 g, 0.134 mol) in methylene chloride (400 ml) at 0 °C. The reaction mixture was stirred for 48 h at room temperature, and then worked up as in above. The crystals were dried at 25 °C/30 mm for 12 h to give 29.7 g (40 %) of the fluoroborate salt **5** as red-brown crystals, m.p. 182 – 184 °C (dec).
Analysis: Calcd. C 66.53; H 7.59; N 3.10. Found: C 66.77; H 7.50; N 2.74.

(all-trans)-1-[9-(4-Methoxy-2,3,6-trimethylphenyl)-3,7-dimethyl-2,4,6,8-nonatetraenylidene]pyrrolidinium hexafluorophosphate (**6**)

To a stirred suspension of 4 Å molecular sieves (20 g) and pyrrolidinium hexafluorophosphate (24 g, 111 mmol) in absolute ethanol (100 ml) under an argon atmosphere was added slowly a solution of aldehyde **3** (23 g, 74 mmol) in methylene chloride (200 ml) at 0 °C. The reaction mixture was stirred for 48 h at room temperature, and then added to methylene chloride (300 ml). The whole mixture was filtered, the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (250 ml), the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 15.7 g (42 %) of the fluorophosphate salt **6** as red-brown crystals, m.p. 181 – 181.5 °C (dec).
Analysis: Calcd. C 58.93; H 6.73; N 2.75; P 6.08. Found: C 58.68; H 6.79; N 2.88; P 5.80.

(all-trans)-1-[2,6,11,15-Tetramethyl-17-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8,10,12,14,16-heptadecaoctaenylidene]pyrrolidinium perchlorate (**8**)

To a stirred suspension of 4 Å molecular sieves (15 g) and pyrrolidinium perchlorate (19 g, 111 mmol) in absolute ethanol (100 ml) under an argon atmosphere was added slowly a solution of β-apo-carotenal **7** (17 g, 40.8 mmol) in methylene chloride (600 ml) at 0 °C. The reaction mixture was stirred for 48 h at room temperature, and then added to methylene chloride (250 ml). The whole mixture was filtered, the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (100 ml), the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 16.2 g (70 %) of the perchlorate salt **8** as purple-black crystals, m.p. 218 – 219 °C.
Analysis: Calcd. C 71.62; H 8.49; N 2.46. Found: C 71.37; H 8.15; N 2.41.

(all-trans)-1-[2,6,11,15-Tetramethyl-17-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8,10,12,14,16-heptadecaoctaenylidene]pyrrolidinium iodide (**9**)

To a stirred suspension of 4 Å molecular sieves (50 g) and pyrrolidinium hydroiodide (64 g, 0.32 mol) in absolute ethanol (250 ml) under an argon atmosphere was added slowly a solution of β-apo-carotenal **7** (120.5 g, 0.289 mol) in methylene chloride (1 l) at 0 °C. The reaction mixture was stirred for 48 h at room temperature, and then added to methylene chloride (500 ml) The whole mixture was filtered, the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (500 ml), the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 91.6 g (53 %) of the iodide salt **9** as blue-black crystals, m.p. 204.5 – 205.5 °C (dec).
Analysis: Calcd. C 68.33; H 8.10; N 2.34; I 21.23. Found: C 63.18; H 7.83; N 2.06; I 25.08.

(all-trans)-1-[2,6,11,15-Tetramethyl-17-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8,10,12,14,16-heptadecaoctaenylidene]pyrrolidinium triiodide (**10**)

To a stirred solution of β-apo-carotenal pyrrolidinium iodide **9** (90 g, 0.15 mol) in methylene chloride (600 ml) under an argon atmosphere was added a solution of iodine (38.2 g, 0.15 mol) in 450 ml of chloroform/methylene chloride (1 : 2) at room temperature. The solution was stirred for additional 12 h, filtered, and concentrated in vacuo to give 127 g (99 %) of the triiodide salt **10** as purple-blue crystals, m.p. 132 – 133 °C (dec).
Analysis: Calcd. C 47.86; H 5.68; N 1.65; I 44.71. Found: C 47.49; H 5.59; N 1.72; I 45.00.

(all-trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)2,4,6,8-nonatetraenylidene]pyrrolidinium chloride (**12**)

To a solution of the retinal pyrrolidinium perchlorate **1** (34.9 g, 79.6 mmol) in methanol (500 ml) was added a solution of rubidium chloride (10.6 g, 87.6 mmol) in methanol (750 ml) at room temperature. The whole mixture was heated to reflux for 3 h, and allowed to cool down. The mixture was stirred for 12 h at room temperature, and then filtered. The filtrate was concentrated in vacuo, redissolved in methylene chloride (250 ml), and filtered to remove undissolved material. The filtrate was concentrated in vacuo to give 25.8 g (86 %) of the chloride salt **12** as an orange-red solid, m.p. 100 °C (dec).
Analysis: Calcd. Cl 9.48. Found: Cl 8.94.

(all-trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium bromide (**13**)

To a solution of the retinal pyrrolidinium perchlorate **1** (30.09 g, 68.7 mmol) in methanol (1 l) was added a solution of rubidium bromide (12.5 g, 75.6 mmol) in methanol (1.25 l) at room temperature. The whole mixture was heated to reflux for 3 h, and then allowed to cool down with stirring at room temperature for 12 h. The mixture was filtered, the solids were washed with ice-cold methanol. The filtrate was concentrated in vacuo, recrystallized from CH_2Cl_2/Ether to give 28.3 g (98 %) of the bromide salt **13** as an orange-red solid, m.p. 162 – 164.0 °C (dec).
Analysis: Calcd. Br 1909. Found: Br 19.33.

(all-trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium tetrafluoroborate (**14**)

To a stirred suspension of 3 Å molecular sieves (15 g) and pyrrolidinium fluoroborate (21.8 g, 0.137 mol) in absolute ethanol (100 ml) under an argon atmosphere was added slowly a solution of crude (30 – 40 %) vitamin A aldehyde (140 g) in absolute ethanol (100 ml) at 0 °C. The reaction mixture was stirred for 1 h at room temperature, and then added to methylene chloride (300 ml). The whole mixture was filtered and the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (100 ml), the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 23 g (40 %) of the tetrafluoroborate salt **14** as dark red crystals, m.p. 185 °C (dec).
Analysis: Calcd. C 67.77; H 8.53; N 3.29. Found: C 67.21; H 8.59; N 3.19.

(all-trans)-1-[3,7-Dimethyl-9(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium hexafluorophosphate (**15**)

To a stirred suspension of 3 Å molecular sieves (40 g) and pyrrolidinium fluorophosphate (51 g, 0.23 mol) in absolute ethanol (200 ml) under an argon atmosphere was added slowly a solution of crude (30 – 40 %) vitamin A aldehyde (225 g) in absolute ethanol (500 ml) at 0 °C. The reaction mixture was stirred for 24 h at room temperature, and then added to methylene chloride (1 l). The whole mixture was filtered and the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (300 ml) and the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 100 g (88 %) of the hexafluorophosphate salt **15** as purple-black crystals, m.p. 200 °C.
Analysis: Calcd. C 59.62; H 7.50; N 2.90; P 6.41. Found: C 59.55; H 7.58; N 2.85; P 6.43.

(all-trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium iodide (**16**)

To a stirred suspension of 4 Å molecular sieves (20 g) and pyrrolidinium hydroiodide (23 g, 0.118 mol) in absolute ethanol (150 ml) under an argon atmosphere was added slowly a solution of crude (30 – 40 %) vitamin A aldehyde (109 g) in absolute ethanol (200 ml) at 0 °C. The reaction mixture was stirred for 12 h at room temperature, and then added to methylene chloride (500 ml). The whole mixture was filtered and the solids were washed with methylene chloride. The filtrate was added to absolute ethanol (700 ml) and the combined solution was heated to distil off the methylene chloride. The solution was then allowed to cool down to room temperature. The precipitate was filtered and washed with absolute ethanol. The crystals were dried at 25 °C/30 mm for 12 h to give 41 g (75 %) of the iodide salt **16** as reddish-brown crystals, m.p. 100 °C (dec).
Analysis: Calcd. C 61.93; H 7.80; N 3.01; I 27.26. Found: C 60.26; H 7.59; N 2.98; I 25.16.

(all-trans)-1-[3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6,8-nonatetraenylidene]pyrrolidinium triiodide (**17**)

To a stirred solution of retinal pyrrolidinium iodide **16** (40 g, 85.9 mmol) in methylene chloride (300 ml) under an argon atmosphere was added a solution of iodine (22 g, 85.9 mmol) in 240 ml of chloroform/methylene chloride (1 : 2) at room temperature. The solution was stirred for 12 h, filtered, and concentrated in vacuo to give brown solids. The solids were dried at 50 °C/30 mm for 12 h to give 57 g (92 %) of the triiodide salt **17** as reddish-brown crystals, m.p. 150 – 151 °C.
Analysis: Calcd. C 40.08; H 5.05; N 1.95; I 52.93. Found: C 39.91; H 4.91; N 1.88; I 52.71.

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