Electrophilic Substitution in Polymethine Dyes; Double Nitration of Bis(dimethylamino) pentamethinium Perchlorate

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Whereas bromination of 1,5-bis (dimethylamino)-pentamethinium perchlorate with *N*-bromosuccinimide in chloroform gives exclusively the 2-bromo derivative, both the 2-nitro and the 2,4-dinitro derivatives are obtained with nitric acid in acetic anhydride. ^{1}H NMR spectroscopy suggests a delocalized all-*anti* chromophore for the 2-bromo derivative, but bond alternation for the 2-nitro derivative. For the latter, UV-spectroscopy suggests a change of conformation going from ethanol to dichloromethane.

X-Ray diffraction of the 2,4-dinitro derivative shows two crystallographically independent cation molecules having the same unsymmetric non-planar conformation, best described as a roughly planar delocalized 1,3-dinitro-*syn*, *anti*-allylic anion chromophore, substituted by two dimethyliminium cationic groups rotated out of the plane of the chromophore.

When 1,5-bis(dimethylamino)pentamethinium perchlorate (*1a*) is dissolved in conc. sulfuric acid, the only species present has the 2-protonated structure *2a*, as revealed by ^{13}C NMR spectroscopy.[1] Replacement of the perchlorate anion with bromide gives initially the same set of nine lines in the ^{13}C spectrum, but along with these a new set of nine lines develops slowly. The solution gives off sulfur dioxide and the old line set becomes finally replaced by the new. Clearly, bromine is formed and the final species was shown[1] to have a bromonium ion added to the 2-position to give *2b*, the dicationic intermediate to be expected in an electrophilic substitution reaction. This observation has led us to study the scope of electrophilic substitution in polymethine dyes.
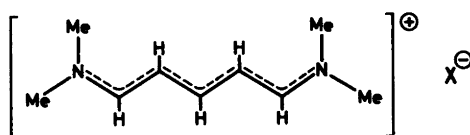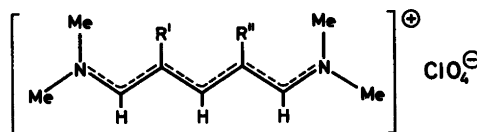
1a: X = ClO₄
1b: X = Br
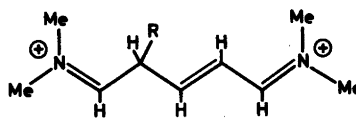
2a: R = H
2b: R = Br

3a: R' = Br , R'' = H
3b: R' = NO₂, R'' = H
3c: R' = NO₂, R'' = NO₂

CHEMICAL ASPECTS

Bromination of polymethine dyes have already been performed by Kučera and Arnold[2] using *N*-bromoacetamide or *N*-bromosuccinimide in chloroform. We have verified that even under forcing conditions only the monosubstituted derivative is formed from 1,5-bis(dimethylamino)pentamethinium perchlorate and confirmed by NMR spectroscopy that in fact the bromine

substituent sits in the 2-position. Also from 1,7-bis(dimethylamino)heptamethinium perchlorate only a monobromo derivative could be obtained. It proved however to be the 4-isomer, presumably because the central 4-position is less hindered than the 2-position.

The same authors also reported[2] that 1,5-bis(dimethylamino) pentamethinium perchlorate can be nitrated, using nitric acid in acetic anhydride, to yield a mononitro derivative, m.p. 187–189 °C. In this case, however, we find that both a mono- and a dinitro derivative can be easily obtained depending on the reaction conditions. Following the published procedure, using three equivalents of nitric acid, a dinitro derivative, m.p. 194–197 °C, is formed exclusively, whereas a mononitro derivative, m.p. 168–171 °C, is the only product when one equivalent is used. The structures were unequivocally proven by ^{1}H NMR spectroscopy, the nitro group occupying the 2-position in the lower melting compound (3b) and the 2- and 4-positions in the higher melting compound (3c). Kučera and Arnold must have collected several crystal crops since their reported melting point is closest to that of our dinitro derivative, although their analysis is perfect for the mononitro derivative. Also, their reported UV spectrum in ethanol (305 nm, ε 8200; 480 nm, ε 14900) is different from that of our mononitro compound (332 nm, ε 4300; 420 nm, ε 29100) and could support a dinitro structure. Instability in ethanol prevented us, however, from obtaining a reliable UV spectrum of the dinitro derivative. In dichloromethane, both compounds are stable and have UV-spectra quite different from those in ethanol, suggesting a solvent-dependent conformational equilibrium.

All these substitution products are too unstable to be chromatographed on alumina. The monobromo and mononitro derivative both give well-defined decomposition products which were shown to be substituted 5-dimethylamino-penta-2,4-dienals resulting from hydrolytic loss of one mol of dimethylammonium perchlorate.

CONFORMATIONAL ASPECTS

The parent 1,5-bis(dimethylamino)penta-methinium cation has been shown to have a planar all-anti conformation in the crystal lattice both when the counter ion is perchlorate[3–5] and

when it is chloride.[6] The observed intermediate ("aromatic") bond character and lack of alternation in the bond lengths of the chromophore suggests equal contribution from both main resonance structures. The persistence of this conformation also in solution is supported by the high value (12 Hz) of the vicinal coupling constants in the ^{1}H NMR spectrum,[7] the presence of two NCH$_3$ lines (coalescence at 80–90 °C, $\Delta G^{\neq} = 76-78$ kJ mol^{-1}),[7] the invariability of the spectrum on cooling and the failure to observe more than one coloured zone on chromatographic columns.[7]

It is to be expected that already a single substituent (in 2-position) would create considerable steric hindrance and force the chromophoric system out of coplanarity, as there are no alternative planar conformations (with one or more syn bonds) without similar steric interactions. With both the 2- and 4-positions substituted, the steric difficulties must increase enormously, and it is not difficult to understand that our attempts to prepare the 2,4-dibromoderivative were unsuccessful. The observation that the dinitro derivative is formed with such ease therefore came as a total surprise.

For the 2-bromo derivative (3a) the extended all-anti chromophore seemed to be essentially intact as witnessed by the high and equal values (12 Hz) of both observable vicinal coupling constants in the ^{1}H NMR spectrum and the presence of four NCH$_3$ signals (two coinciding).

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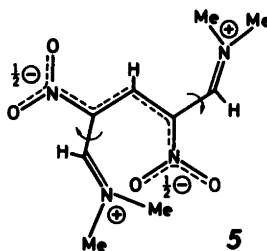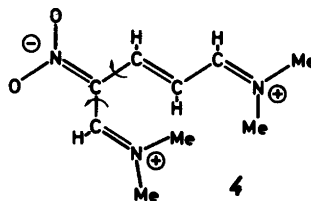
We conclude that minor deviations from planarity may be evenly distributed all through the chromophore and that electronic through-conjugation is largely retained, as also witnessed by the presence of a single strong UV maximum at 414 nm (ε 75700) for *3a* as compared to 412 nm (ε 118900) for *1a*.[2]

For the *2-nitro derivative* (*3b*) on the other hand the vicinal coupling constants are not equal, one being larger (14 Hz, suggesting *trans* coupling across a double bond) and the other smaller (10–11 Hz, suggesting *anti* coupling across a single bond). A planar *syn* relationship for the latter seems less probable as this is known to give a smaller *J*-value (~8 Hz).[8] The presence of four NCH$_3$ signals (two coinciding) shows that high double-bond character resides in the terminal CN bonds, hence also in the C3C4 bond, while the C4C5 bond must then have single-bond character. We conclude that the conjugating power of the nitro group dominates this chromophoric system. Structure *4* is proposed as the main resonance form, producing single-bond character in the C4C5 bond and double-bond character in the C3C4 bond as required by the *J* values. To relieve steric strain, rotation can occur about one or both single bonds C1C2 or C2C3. Rotation only about C1C2 leaves an extended planar 1-dimethylamino-4-nitrobuta-1,3-diene chromophore carrying a dimethyliminium substituent, whereas rotation only about C2C3 leaves a shorter planar 1-dimethylamino-2-nitroethylene chromophore carrying a vinylogous dimethyliminium substituent. The presence of two such conformers could explain our observation of two UV maxima in ethanol, one at longer wavelength (420 nm, ε 29100), the other at shorter wavelength (332 nm, ε 4300). For comparison, 1-dimethylamino-4-nitrobuta-1,3-diene itself is known to be orange,[9] and 1-dimethylamino-2-nitroethylene itself is yellow with UV maximum at 354 nm (ε 25300).[10] The intermediate position
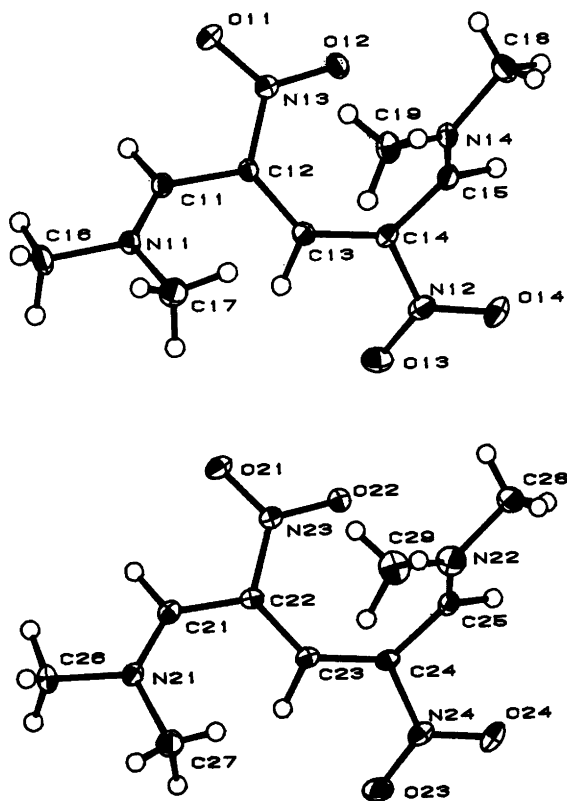

Fig. 1. ORTEP plots of the two independent 1,5-bis(dimethylamino)-2,4-dinitropentamethinium ions.

in CH_2Cl_2 at 404 nm (ε 47300) could arise from a compromise conformation caused by tight ion pairing in this solvent.

Structural information from the NMR spectrum of the *dinitro derivative* (*3c*) is very limited since there are no vicinally related protons. The presence of only two lines for methine protons corresponds to the chemical symmetry, and could conceal a rapidly averaged conformational asymmetry. The low-field position of the 1- (and 5-) protons and the presence of two NCH₃ signals

indicates that the CN bonds have strong double-bond character. As there are altogether ten possible ways in which *anti* and *syn* conformation in the four CC bonds can be combined, none of which can be physically realized as a coplanar system, it seemed virtually impossible to predict in which way the molecule would minimize its inherent strain. The crystal structure was therefore determined by X-ray diffraction.

Table 1. Fractional atomic coordinates.

Atom	x	y	z	Atom	x	y	z
Cl1	0.41124(0)	0.97973(3)	0.16006(0)	C23	0.2909(2)	0.3934(1)	0.7087(1)
Cl2	0.60122(6)	0.27702(3)	0.37620(5)	C24	0.3260(2)	0.4708(1)	0.7316(1)
O1	0.4211(2)	0.9190(1)	0.2274(1)	C25	0.3947(2)	0.5114(1)	0.8173(1)
O2	0.5330(2)	1.0043(1)	0.1718(1)	C26	0.1153(2)	0.1535(1)	0.6180(1)
O3	0.3499(2)	0.9475(1)	0.0692(1)	C27	0.0595(2)	0.2952(1)	0.6105(2)
O4	0.3455(3)	1.0459(1)	0.1733(1)	C28	0.4577(2)	0.5400(1)	0.9777(1)
O5	0.4933(2)	0.2843(1)	0.3958(1)	C29	0.2746(2)	0.4548(1)	0.8961(2)
O6	0.6129(2)	0.3453(1)	0.3250(1)	H11	0.704	0.530	0.834
O7	0.7083(2)	0.2691(2)	0.4586(2)	H13	0.789	0.347	0.927
O8	0.5877(2)	0.2081(1)	0.3197(2)	H15	0.574	0.150	0.753
O11	0.5668(1)	0.4855(1)	0.6961(1)	H21	0.310	0.199	0.738
O12	0.5303(1)	0.3584(1)	0.6958(1)	H23	0.239	0.386	0.642
O13	0.7685(2)	0.2387(1)	1.0022(1)	H25	0.460	0.550	0.820
O14	0.6999(2)	0.1393(1)	0.9077(1)	H161	0.855	0.607	0.923
O21	0.4482(2)	0.2445(1)	0.8754(1)	H162	0.983	0.592	0.911
O22	0.4882(1)	0.3701(1)	0.8730(1)	H163	0.967	0.564	1.001
O23	0.2292(2)	0.5025(1)	0.5760(1)	H171	0.936	0.393	0.861
O24	0.3249(2)	0.5957(1)	0.6725(1)	H172	1.012	0.421	0.962
N11	0.8749(2)	0.4960(1)	0.8916(1)	H173	1.028	0.467	0.881
N12	0.7252(2)	0.2107(1)	0.9238(1)	H181	0.515	0.166	0.605
N13	0.5952(2)	0.4177(1)	0.7299(1)	H182	0.625	0.161	0.573
N14	0.6601(2)	0.2299(1)	0.6853(1)	H183	0.541	0.233	0.559
N21	0.1536(2)	0.2345(1)	0.6528(1)	H191	0.828	0.281	0.739
N22	0.3757(2)	0.5029(1)	0.8914(1)	H192	0.742	0.325	0.661
N23	0.4227(2)	0.3111(1)	0.8391(1)	H193	0.791	0.250	0.642
N24	0.2912(2)	0.5257(1)	0.6546(1)	H261	0.192	0.119	0.648
C11	0.7589(2)	0.4853(1)	0.8469(1)	H262	0.101	0.153	0.553
C12	0.7026(2)	0.4098(1)	0.8114(1)	H263	0.050	0.137	0.636
C13	0.7359(2)	0.3402(1)	0.8636(1)	H271	0.069	0.336	0.648
C14	0.7002(2)	0.2620(1)	0.8447(1)	H272	−0.018	0.271	0.599
C15	0.6373(2)	0.2207(1)	0.7594(1)	H273	0.062	0.314	0.551
C16	0.9226(2)	0.5726(1)	0.9359(1)	H281	0.520	0.573	0.965
C17	0.9708(2)	0.4377(1)	0.9003(2)	H282	0.498	0.501	1.015
C18	0.5781(2)	0.1954(1)	0.5986(1)	H283	0.411	0.572	1.002
C19	0.7618(2)	0.2778(1)	0.6829(1)	H291	0.213	0.445	0.832
C21	0.2619(2)	0.2466(1)	0.7164(1)	H292	0.239	0.479	0.935
C22	0.3178(2)	0.3205(1)	0.7551(1)	H293	0.298	0.405	0.920

CRYSTAL STRUCTURE OF 1,5-BIS(DIMETHYLAMINO)-2,4-DINITRO-PENTAMETHINIUM PERCHLORATE

The structure was solved by direct methods (see Experimental). Final fractional coordinates are given in Table 1 and structural data in Table 2. ORTEP drawings of the two independent organic cations are presented in Fig. 1. The numbering of the atoms corresponds to that given in the tables.

With eight formula units in the cell there are two crystallographically independent ions of each kind.

The *perchlorate ions* are uncoordinated in the crystal. The C1−O distances are more equal than what is found in hydrates, and the arrangements of oxygen atoms are close to tetrahedral. The mean C1−O bond length around C11 is 1.460 Å and around C12 1.464 Å, the values are corrected for thermal motion. The O−C1−O angles range from 107.8 to 111.0°.

The *pentamethinium ions* have a very unsymmetric non-planar structure. Being essentially the same for the two crystallographically independent ions (Table 2), it seems likely that this conformation could represent an energy minimum also in solution. The main carbon skeleton is nearly planar, and can be described as *syn, anti* about the adjacent central bonds, (average torsion angles 13 and −177°). The average bond lengths are 1.38 and 1.40 Å; hence these have one-and-a-half bond character. On the other hand, the two outer CC-bonds are much longer (average lengths 1.45 and 1.44 Å) and correspond essentially to single bonds between sp^2 carbons. Furthermore, the CN-bonds to the dimethylamino groups are so short (average lengths 1.29 and 1.30 Å as compared with 1.34 Å for the unsubstituted pentamethinium ion)[3−6] that both are to be considered as localized CN double bonds carrying full positive charge. Both dimethyliminium groups are also rotated out of the plane of the carbon skeleton (average torsion angles 36° and 45°). There is a correlation between the torsion angles and the corresponding bond lengths (Table 2), the CC bond lengths varying from 1.372 to 1.453 Å as the torsion angles vary from 9 to 47°.

All this leads to the conclusion that the dimethyliminium groups act as nonconjugated substituents on a central chromophore carrying

one compensating negative charge stabilized by the two nitro groups. In accord with this is the observed considerable shortening of the CN-bonds to the nitro groups (average lengths 1.45 and 1.43 Å as compared with 1.49 Å in nitrobenzene[11]), and the near coplanarity of both nitro groups with the intervening three-carbon system, all *syn* torsion angles in these CN bonds being smaller than 10°. Thus, structure **5** would be the best valency-bond description of this cation. The conjugated chromophoric system can actually be considered as an allylic 1,3-dinitropropenide anion, and it is only the two charged substituents which convert it to a net cationic species.

The unsubstituted 1,3-dinitro propenide anion chromophore is not known in any stable molecule, but has been postulated as a transient species observed by UV-spectroscopy in the reaction, between 1,3,5-nitrobenzene and sodium methoxide.[12] Its absorption maximum (482 nm, ε 24000) fits well with that observed by Kučera and Arnold[2] and assigned by us to the dinitro compound **3c**.

The main intramolecular interactions determining the degree of non-planarity are between the 1-dimethyliminium and the 4-nitro group linked through the *syn* C2C3 bond, and between the central methine group and one N−CH$_3$ group from each end.

There is also a considerable amount of valency angle strain in the molecule, especially at the *syn* C2C3 bond where the CCC angles are found in the range 130−135°.

EXPERIMENTAL

1,5-Bis(dimethylamino)-2-bromopentamethinium perchlorate. This was prepared as described.[2]

^{1}H NMR (CD$_3$CN) δ 7.61 (1H,d,*J* 12), 7.45 (1H,s), 7.42 (1H,d,*J* 12), 5.84 (1H,t,*J* 12), 3.35 (6H,s), 3.27 (3H,s) and 3.10 (3H,s). The substance is unstable on alumina. A yellow solid is eluted which is identified by ^{1}H NMR-spectroscopy as 5-dimethylamino-2-bromopenta-2,4-dienal.

^{1}H NMR (CD$_3$OH): δ 8.82 (1H,s), 7.37 (1H, d,*J* 11), 7.13 (1H,d,*J* 11), 5.38 (1H,t,*J* 11) and 2.98 (6H,s).

1,5-Bis(dimethylamino)-2-nitropentamethinium perchlorate. To a stirred and cooled solution of 1,5-bis(dimethylamino)pentamethinium per-

Table 2. Structural data.

Bond lengths (Å)		corr.	Bond angles (°)			
Cl 1 O 1	1.447(2)	1.465	O 1	Cl 1	O 2	108.6(1)
Cl 1 O 2	1.437(2)	1.467	O 1	Cl 1	O 3	109.4(1)
Cl 1 O 3	1.439(2)	1.460	O 1	Cl 1	O 4	109.7(1)
Cl 1 O 4	1.418(2)	1.446	O 2	Cl 1	O 3	109.0(1)
Cl 2 O 5	1.430	1.449	O 2	Cl 1	O 4	109.4(1)
Cl 2 O 6	1.443	1.468	O 3	Cl 1	O 4	110.7(1)
Cl 2 O 7	1.422	1.463	O 5	Cl 2	O 6	110.0(1)
Cl 2 O 8	1.434	1.477	O 5	Cl 2	O 7	111.0(1)
			O 5	Cl 2	O 8	108.2(1)
			O 6	Cl 2	O 7	110.0(1)
			O 6	Cl 2	O 8	107.8(1)
			O 7	Cl 2	O 8	109.7(2)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
N11 C16	1.470(2)	1.472(3)	C16 N11 C17	113.9(2)	114.0(2)
N11 C17	1.463(3)	1.464(3)	C11 N11 C16	120.8(2)	120.1(2)
N11 C11	1.286(3)	1.297(3)	C11 N11 C17	125.2(2)	125.9(2)
C11 C12	1.440(3)	1.427(3)	N11 C11 C12	124.6(2)	128.3(2)
C12 N13	1.417(2)	1.427(3)	C11 C12 C13	121.8(2)	124.4(2)
C12 C13	1.397(3)	1.400(3)	C11 C12 N13	112.6(2)	113.0(2)
N13 O11	1.249(2)	1.241(2)	N13 C12 C13	124.1(2)	121.4(2)
N13 O12	1.244(2)	1.243(2)	C12 N13 O11	118.0(2)	119.7(2)
C13 C14	1.379(3)	1.372(3)	C12 N13 O12	120.0(2)	118.7(2)
C14 C15	1.439(3)	1.448(3)	O11 N13 O12	122.0(2)	121.6(2)
C14 N12	1.449(2)	1.453(2)	C12 C13 C14	132.9(2)	135.2(2)
N12 O13	1.234(2)	1.232(2)	C13 C14 C15	131.7(2)	134.0(2)
N12 O14	1.241(2)	1.240(2)	C13 C14 N12	116.1(2)	115.1(2)
C15 N14	1.294(2)	1.284(2)	N12 C14 C15	112.2(2)	110.9(2)
N14 C18	1.465(3)	1.467(3)	C14 N12 O13	120.3(2)	120.4(2)
N14 C19	1.465(3)	1.468(3)	C14 N12 O14	116.6(2)	116.9(2)
			O13 N12 O14	123.1(2)	122.8(2)
			C14 C15 N14	124.5(2)	124.5(2)
			C15 N14 C18	120.3(2)	120.9(2)
			C15 N14 C19	124.0(2)	122.9(2)
			C18 N14 C19	115.5(2)	116.1(2)

Torsion angles(°)

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C16 N11 C11 C12	−171.8(2)	−176.3(2)	C12 C13 C14 C15	16.3(4)	9.2(4)
C17 N11 C11 C12	11.3(3)	4.8(3)	C12 C13 C14 N12	−161.3(2)	−168.9(2)
N11 C11 C12 C13	44.4(3)	28.0(3)	C13 C14 N12 O13	4.7(3)	3.4(3)
N11 C11 C12 N13	−149.0(2)	−164.4(2)	C13 C14 N12 O14	−176.0(2)	177.8(2)
C11 C12 N13 O11	4.3(2)	7.4(3)	C15 C14 N12 O13	−173.3(2)	178.1(2)
C11 C12 N13 O12	−173.4(2)	−170.9(2)	C15 C14 N12 O14	6.0(2)	− 0.8(2)
C13 C12 N13 O11	170.6(2)	175.4(2)	C13 C14 C15 N14	42.5(3)	47.4(3)
C13 C12 N13 O12	− 7.1(3)	− 2.8(3)	N12 C14 C15 N14	−139.4(2)	−134.5(2)
C11 C12 C13 C14	−177.2(2)	−175.9(2)	C14 C15 N14 C18	−169.8(2)	−173.7(2)
N13 C12 C13 C14	17.7(3)	17.5(3)	C14 C15 N14 C19	6.5(3)	4.5(3)

chlorate (210 mg, 0.83 mmol) in acetic anhydride (3.5 ml) was added 68 % nitric acid (0.06 ml, 0.91 mmol). After 30 min. at 0 °C the reaction mixture was stirred for a further 2 h at 20 °C and then evaporated to dryness under oilpump vacuum. The residue was crystallized from acetic anhydride and the solid dried in vacuum. Recrystallization from a slowly evaporating mixture of acetonitrile and toluene afforded yellow crystals, m.p. 168–171 °C (94 mg, 38 %). Found: C 35.9; H 5.3; N 14.2. Calc. for $C_9H_{16}ClN_3O_6$: C 36.3; H 5.4; N 14.1. UV (CH_2Cl_2): 404 nm (ε 47300). UV (ethanol): 332 nm (ε 4300), 420 nm (ε 29100).

^{1}H NMR (CD_3CN): δ 8.44 (1H,s), 8.00 (1H,d,J 11), 7.58 (1H,d,J 14), 6.67 (1H,q,J 11,14) 3.50 (3H,s), 3.40 (3H,s) and 3.29 (6H,s).

The substance is unstable on alumina. A yellow solid is eluted which is identified as 5-dimethylamino-nitropenta-2,4-dienal.

Found: C 49.6; H 6.0; N 15.7. Calc. for $C_7H_{10}N_2O_3$: C 49.4; H 5.9; N 16.5 The ^{1}H NMR spectrum suggests a mixture of the two isomers having the nitro group in 2- and in 4-position.

1,5-Bis(dimethylamino)-2,4-dinitropentamethinium perchlorate. To a solution of 1,5-bis-(dimethylamino)pentamethinium perchlorate (400 mg, 1.6 mmol) in acetic anhydride (7 ml) was added 68 % nitric acid (0.32 ml, 4.85 mmol) as described for the 2-nitro-derivative. Crystallization from acetic anhydride gave a yellow solid, m.p. 194–197 °C (104 mg, 19 %).

Found: C 32.0; H 4.4; N 16.0. Calc. for $C_9H_{15}ClN_4O_8$: C 31.5; H 4.4; N 16.4. UV (CH_2Cl_2): 349 nm (ε 8000), 421 nm (ε 15700). No meaningful spectrum was obtained in ethanol. ^{1}H NMR (CD_3CN): δ 8.70 (2H,s), 8.30 (1H,s), 3.31 (6H,s) and 3.68 (6H,s). The substance becomes black on storage.

X-Ray crystallography of 1,5-bis(dimethylamino)-2,4-dinotropentamethinium perchlorate. Crystals were formed by recrystallization from a slowly evaporating mixture of 1,2-dichloroethane and acetonitrile. Data for unit cell determination and intensity data were collected using a SYNTEX P $\bar{1}$ four-circle diffractometer, MoKα radiation (λ=0.71069 Å). The temperature at the crystal site was kept at −150 °C; specimen dimension 0.3×0.4×0.4 mm. The $\theta/2\theta$ scan technique was employed with scan speed (2θ) 2−4° min^{-1} depending on the intensity, and scan range 2.2°. 4696 independent reflections with sin θ/λ≤0.76 Å^{-1} were measured; of these 4570 had $I/\sigma(I)$>2.5 and were used for the structure analysis. The intensity data were corrected for Lorentz and polarization effects; no absorption or extinction corrections were applied. Atomic form factors used were those of Doyle and Turner[13] for Cl,O,N and C, and of Stewart,

Davidson and Simpson,[14] for H. A description of the computer programs employed is given by Groth.[15]

Crystal data. 1,5-Bis(dimethylamino)-2,4-dinitropentamethinium perchlorate, $C_9H_{15}N_4O_8Cl$, monoclinic, a=11.812(2) Å; b=16.818(3) Å; c=15.805(3) Å; β=113.04(1); V=2889.2 Å^3 (t=−150 °C). $F(000)$=1424; Z=8; $F.W.$=342.69; D_x=1.573 g cm^{-1}; μ(MoKα)=3.2 cm^{-1}. Absent reflections: $h\,k\,l$ for $h+k$ odd, $h0l$ for l odd. Space group Cc (No. 9).

Structure determination. The structure was solved by direct methods[16] and refined by block diagonal and full-matrix least-squares calculations. Non-hydrogen atoms were given anisotropic temperature factors; positional parameters for hydrogen atoms were refined. Weights for the least-squares calculations were the inverse of the variance of the observed intensities, taken as $\sigma^2(I)$=C_T+$(0.02\ C_N)^2$ where C_T is the total number of counts and C_N the net count. The refinements terminated with a conventional R-value of 0.032, R_w=0.035 and S= $[\Sigma w(\Delta F^2)/(n-m)]^{1/2}$=1.76.

Final fractional coordinates are given in Table 1. Thermal parameters and the structure factor listing may be obtained from the authors. Structural data are listed in Table 2; estimated standard deviations are calculated from the variance−covariance matrix.

ORTEP drawings of the two independent organic ions are presented in Fig. 1. The numbering of the atoms corresponds to that given in the tables.

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