there is no change in π-electron delocalization to the nitro group by salt formation. This is a difference from the related compounds nitromalonamide (Simonsen & Thorup, 1979) and its ammonium salt (Simonsen, 1981) where the C—NO_2 distances are 1·397 (4) and 1·327 (4) Å respectively.

The anions are connected in infinite chains by pairs of N—H···O hydrogen bonds grouped around centres of symmetry (Fig. 2). These hydrogen bonds may contribute to the low solubility of the title compound (0·072 g in 100 ml H_2O, 296 K). The N···O distances involved range from 2·825 (2) to 2·831 (2) Å. The distances from the ammonium N atom to the surrounding O atoms range from 2·935 (2) to 3·068 (2) Å.

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2,4-Bis(dimethylamino)-6-phenyl-1,3,5-thiadiazinium Tetraphenylborate, $C_{13}H_{17}N_4S^+.C_{24}H_{20}B^-$

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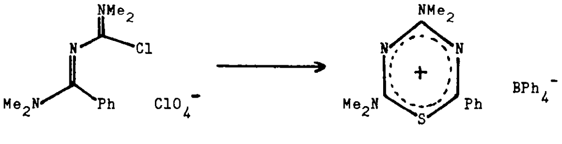
Abstract. $M_r = 580\cdot6$, monoclinic, $P2_1/a$, $a = 26\cdot076$ (13), $b = 9\cdot517$ (5), $c = 13\cdot046$ (7) Å, $\beta = 102\cdot11$ (2)°, $V = 3165\cdot5$ (29) Å^3, $Z = 4$, $D_x = 1\cdot218$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 1\cdot125$ mm^{-1}, $F(000) = 1232$, $T = 293$ (1) K, final $R = 0\cdot057$ for 3899 significant reflections. In the almost planar 1,3,5-thiadiazinium moiety the endocyclic bond lengths indicate delocalization of electron density over the atomic centres, C(2), N(3), C(4), together with the exocyclic N atoms of the dimethylamino substituents [average C—N distance = 1·321 (9) Å], and a double bond of length 1·281 (4) Å between N(5) and C(6). The geometry of the tetraphenylborate anion is normal and there are no non-bonded contacts less than the sum of the respective van der Waals radii.

Introduction. We recently reported that 1-chloro-1,3-bis(dimethylamino)-3-phenyl-2-azapropenylium perchlorate (I) reacted with potassium thiocyanate, followed by sodium tetraphenylborate, to yield the rearranged 1,3,5-thiadiazinium salt (II), whose structure was confirmed by X-ray analysis (Boyd, Lindley & Nicolaou, 1984). Since, to our knowledge this is the first determination of the structure of a 1,3,5-thiadiazinium salt, we present in this paper details of our work.



(I) (II)

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Experimental. Material prepared by stirring a solution of the perchlorate (I) (0·4 g) in acetonitrile (10 ml) with potassium thiocyanate (0·115 g, 1 mol) for 1 h, filtering from the precipitated solid, evaporating the filtrate under reduced pressure and treating the resulting oil with a solution of sodium tetraphenylborate (0·40 g) in water (20 ml). 2,4-Bis(dimethylamino)-6-phenyl-1,3,5-thiadiazinium tetraphenylborate (0·42 g, 61%) crystallized from dichloromethane–ethyl acetate. Spectral parameters: $\nu_{\rm max}$(Nujol) 1602, 1579, 735 and 708 cm^{-1}; δ(CD_3CN) 3·19 (*s*,*N*-Me), 3·33 (*s*,*N*-Me), 3·36 (*s*,*N*-Me), 3·51 (*s*,*N*-Me), 6·80–7·30 (*m*, 20H, 4 × Ph), 7·66 (*m*, 3H) and 8·15 (*m*, 2H, Ph). Red prismatic crystals, m.p. 489 K. Crystal fragment, 0·19 × 0·39 × 0·26 mm, mounted along **b**; preliminary crystal data from precession photographs. Hilger & Watts Y290 diffractometer, Cu $K\alpha$ nickel-filtered radiation, 20 reflections used for accurate measurement of cell parameters. $\omega/2\theta$ step scans, 0·02° per step, count time 1 s per step, moving-window (Tickle, 1975) estimation of intensity, 40 out of 60 steps, and background. Four reference reflections every 50 reflections, intensity variation 3·8%. Intensity data for $1 \le \theta \le 25°$ (4 equivalents) and $25 \le \theta \le 65°$ (1 equivalent), $-30 \le h \le 30$, $0 \le k \le 10$, $0 \le l \le 15$. Total of 6821 measurements, agreement residual for 2349 equivalents of 2·8%, 4731 independent reflections of which 3899 had $I \ge 3\sigma(I)$. Lp and empirical absorption correction from 020 and 060 reflections (North, Phillips & Mathews, 1968) for all data; max. variation in transmission factor of 21·7%. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement [modified program of D. W. J. Cruickshank and J. G. F. Smith (Cruickshank, 1965)] using only significant reflections, isotropic, $R = 0·141$. H atoms located by difference Fourier synthesis but subsequently constrained in geometricized positions, C—H 1·0 Å. Further refinement with all non-H atoms anisotropic, but thiadiazinium and tetraphenylborate ions refined in alternate cycles (max. variable parameters = 226, including an overall scale factor), final $R = 0·057$ (0·069 for all 4731 unique *hkl*), $wR = 0·075$. Quantity minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 0·01$ if $|F_o| \le 15$ otherwise $w = [1-\exp(-20\sin^2\theta/\lambda^2)]/(20 + |F_o| + 0·002|F_o|^2)$. Max. $\Delta/\sigma = 0·41$; max., min. heights in final difference Fourier map 0·2, −0·2 e Å^{-3}. Scattering factors from Hanson, Herman, Lea & Skillman (1964); all computations carried out on the CDC 6600 computer at the University of London Computer Centre.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3) *of the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$†
S(1)	0·02472 (3)	0·10751 (9)	0·19644 (5)	49·6 (3)
C(2)	0·0855 (1)	0·1697 (3)	0·2647 (2)	42 (1)
N(3)	0·1151 (1)	0·2602 (3)	0·2277 (2)	46 (1)
C(4)	0·1014 (1)	0·3102 (3)	0·1305 (2)	43 (1)
N(5)	0·0540 (1)	0·2895 (3)	0·0598 (2)	49 (1)
C(6)	0·0196 (1)	0·2053 (3)	0·0822 (2)	42 (1)
N(21)	0·1019 (1)	0·1186 (3)	0·3601 (2)	53 (1)
C(22)	0·0731 (1)	0·0128 (4)	0·4057 (3)	65 (2)
C(23)	0·1501 (2)	0·1733 (5)	0·4270 (3)	83 (2)
N(41)	0·1357 (1)	0·3895 (3)	0·0957 (2)	49 (1)
C(42)	0·1872 (1)	0·4207 (4)	0·1622 (3)	57 (1)
C(43)	0·1252 (2)	0·4491 (5)	−0·0103 (3)	78 (2)
C(61)	−0·0300 (1)	0·1858 (4)	0·0035 (2)	49 (1)
C(62)	−0·0687 (1)	0·0932 (4)	0·0186 (3)	58 (2)
C(63)	−0·1134 (1)	0·0760 (5)	−0·0597 (3)	68 (2)
C(64)	−0·1198 (1)	0·1533 (5)	−0·1505 (3)	73 (2)
C(65)	−0·0824 (2)	0·2442 (5)	−0·1662 (3)	84 (2)
C(66)	−0·0369 (2)	0·2607 (5)	−0·0899 (3)	75 (2)
B(1)	0·3620 (1)	0·2871 (3)	0·3205 (2)	37 (1)
C(101)	0·3692 (1)	0·4574 (3)	0·3020 (2)	36 (1)
C(102)	0·3264 (1)	0·5471 (3)	0·2694 (2)	48 (1)
C(103)	0·3310 (1)	0·6905 (4)	0·2572 (3)	60 (1)
C(104)	0·3797 (2)	0·7527 (4)	0·2764 (3)	64 (2)
C(105)	0·4236 (1)	0·6686 (4)	0·3076 (3)	58 (1)
C(106)	0·4180 (1)	0·5241 (3)	0·3196 (2)	44 (1)
C(201)	0·3396 (1)	0·2576 (3)	0·4279 (2)	37 (1)
C(202)	0·3012 (1)	0·3413 (3)	0·4572 (2)	48 (1)
C(203)	0·2788 (1)	0·3114 (4)	0·5424 (3)	57 (1)
C(204)	0·2938 (1)	0·1934 (4)	0·6018 (3)	59 (2)
C(205)	0·3314 (1)	0·1072 (2)	0·5762 (2)	58 (1)
C(206)	0·3534 (1)	0·1388 (3)	0·4909 (2)	48 (1)
C(301)	0·3185 (1)	0·2229 (3)	0·2216 (2)	36 (1)
C(302)	0·3129 (1)	0·2748 (3)	0·1199 (2)	43 (1)
C(303)	0·2768 (1)	0·2187 (4)	0·0346 (2)	51 (1)
C(304)	0·2460 (1)	0·1073 (4)	0·0490 (2)	57 (1)
C(305)	0·2513 (1)	0·0511 (4)	0·1477 (3)	62 (1)
C(306)	0·2868 (1)	0·1089 (3)	0·2324 (2)	50 (1)
C(401)	0·4187 (1)	0·2062 (3)	0·3273 (2)	35 (1)
C(402)	0·4300 (1)	0·1263 (3)	0·2458 (2)	47 (1)
C(403)	0·4771 (1)	0·0575 (4)	0·2514 (3)	57 (1)
C(404)	0·5158 (1)	0·0649 (4)	0·3406 (3)	56 (1)
C(405)	0·5070 (1)	0·1439 (4)	0·4236 (3)	56 (1)
C(406)	0·4596 (1)	0·2128 (3)	0·4165 (2)	48 (1)

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

Table 2. *Molecular geometry for the thiadiazinium ion*

All e.s.d.'s include cell-parameter errors.

(*a*) Intramolecular bond lengths (Å)

S(1)–C(2)	1·751 (3)	N(21)–C(23)	1·467 (6)
S(1)–C(6)	1·738 (3)	N(41)–C(42)	1·468 (5)
C(2)–N(3)	1·314 (4)	N(41)–C(43)	1·466 (5)
C(2)–N(21)	1·321 (5)	C(61)–C(62)	1·385 (5)
N(3)–C(4)	1·331 (4)	C(61)–C(66)	1·390 (5)
C(4)–N(5)	1·393 (4)	C(62)–C(63)	1·389 (5)
C(4)–N(41)	1·321 (4)	C(63)–C(64)	1·375 (6)
N(5)–C(6)	1·281 (4)	C(64)–C(65)	1·351 (6)
C(6)–C(61)	1·485 (4)	C(65)–C(66)	1·388 (7)
N(21)–C(22)	1·456 (5)		

(*b*) Angles (°)

C(2)–S(1)–C(6)	98·8 (1)	C(2)–N(21)–C(23)	119·8 (3)
S(1)–C(2)–N(3)	125·0 (2)	C(22)–N(21)–C(23)	117·0 (3)
S(1)–C(2)–N(21)	115·8 (2)	C(4)–N(41)–C(42)	120·9 (3)
N(3)–C(2)–N(21)	119·2 (3)	C(4)–N(41)–C(43)	122·6 (3)
C(2)–N(3)–C(4)	121·5 (3)	C(42)–N(41)–C(43)	116·5 (3)
N(3)–C(4)–N(5)	127·2 (3)	C(6)–C(61)–C(62)	122·4 (3)
N(3)–C(4)–N(41)	117·8 (3)	C(6)–C(61)–C(66)	118·4 (3)
N(5)–C(4)–N(41)	115·1 (3)	C(62)–C(61)–C(66)	119·1 (3)
C(4)–N(5)–C(6)	120·3 (3)	C(61)–C(62)–C(63)	119·6 (3)
S(1)–C(6)–N(5)	126·8 (2)	C(62)–C(63)–C(64)	120·1 (4)
S(1)–C(6)–C(61)	115·1 (2)	C(63)–C(64)–C(65)	120·8 (4)
N(5)–C(6)–C(61)	118·1 (3)	C(64)–C(65)–C(66)	119·9 (4)
C(2)–N(21)–C(22)	123·1 (3)	C(61)–C(66)–C(65)	120·3 (4)

(*c*) Endocyclic torsion angles (°)

S(1)–C(2)–N(3)–C(4)	−2·3 (5)	C(4)–N(5)–C(6)–S(1)	0·0 (5)
C(2)–N(3)–C(4)–N(5)	7·5 (5)	N(5)–C(6)–S(1)–C(2)	3·5 (3)
N(3)–C(4)–N(5)–C(6)	−6·3 (5)	C(6)–S(1)–C(2)–N(3)	−2·4 (3)

Discussion. The positional and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1.* Selected intramolecular bond lengths and angles are listed in Table 2, together with further details of the molecular geometry. Fig. 1 is a schematic drawing of the thiadiazinium ion showing the atomic numbering; Fig. 2 is a stereoscopic drawing of the asymmetric unit viewed along *z*.

In the thiadiazinium ion the S(1)—C(2) and S(1)—C(6) distances, 1·751 (3) and 1·738 (3) Å respectively, are typical of single bonds involving S and sp^2-hybridized C atoms [for example, 1·743 (5) Å in 4a,5,6,7,8,8a-hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1*H*-pyrido[4,3-*e*][1,3,4]thiadiazine (Boyd, Norris & Lindley, 1976) or 1·755 (3) Å in *cis*-3a,6a-dihydro-3a,5,6,6a-tetraphenyl-2-phenylazo-4*H*-cyclopentathiazol-4-one (Boyd, Norris & Lindley, 1977)]. The N(5)—C(6) separation, 1·281 (4) Å, indicates a bond order of two and the corresponding torsion angle C(4)—N(5)—C(6)—S(1) is 0·0 (5)°. However, the endocyclic C(2)—N(3) and N(3)—C(4) distances, together with those for the exocyclic C(2)—N(21) and C(4)—N(41) bonds [mean C—N separation 1·321 (9) Å], suggest delocalization of electron density over this region of the ion so that the formal positive charge can be placed as indicated in Fig. 1. In accordance with this delocalization the geometry at both the dimethylamino substituents is very nearly planar; N(21) and N(41) are displaced by 0·019 (3) and −0·007 (3) Å respectively out of the planes defined by C(2), C(22), C(23) and C(4), C(42), C(43). Indeed the entire thiadiazinium ion including the C(2)- and C(4)-dimethylamino and C(6)-phenyl substituents is almost planar, so that the maximum displacement of an atom out of the plane defined by the six ring atoms is 0·297 (6) Å for C(43). Within the thiadiazinium ring itself the dominant symmetry element is a mirror plane through S(1) and C(4) (see torsion angles in Table 2*c*), indicating a minimal sofa conformation with C(4) displaced by 0·055 (4) Å out of the ring plane; the phenyl substituent at C(6) makes a dihedral angle of 1·8 (3)° with this plane.

The geometry of the tetraphenylborate ion is closely similar to that observed in the corresponding potassium and tetramethylammonium salts (Hoffmann & Weiss, 1974). The B—phenyl distances, average 1·651 (7) Å in the present compound, compare with values of 1·643 (3) Å in the potassium salt and 1·641 (3) Å in the tetramethylammonium salt respectively; the phenyl—B—phenyl angles range between 107·1 (4) and 111·2 (4)°. In all three compounds the endocyclic phenyl angles at the C atoms directly bonded to B are appreciably less than the normal value of 120°, an effect presumably caused by steric crowding of the bulky phenyl groups about the B atom; in the present compound the values for these angles range from 114·3 (4) to 115·3 (4)°.

In the crystal structure there are no non-bonded contacts significantly less than the sum of the respective van der Waals radii.

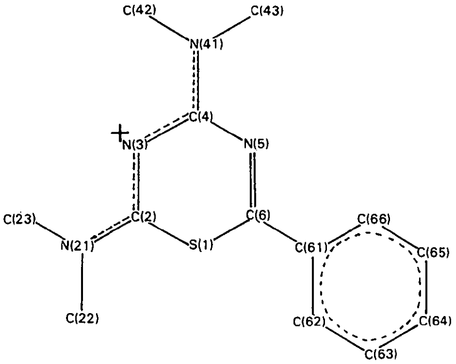

Fig. 1. A schematic drawing of the thiadiazinium ion showing the atomic-numbering scheme.

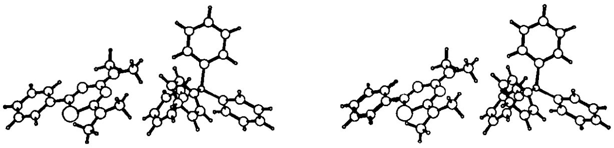

Fig. 2. A stereoscopic drawing of the asymmetric unit viewed along *z*.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and complete bond length and angle data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42223 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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