and used in refinement. Structure solved using program package *SHELXTL* (Nicolet XRD Corp., Freemont, CA) version of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); positional and anisotropic thermal parameters for non-hydrogen atoms refined, based on F, by blocked-cascade least squares, all hydrogen atoms located from difference Fourier map. Hydrogen atoms fixed at idealized (C—H = 0·96 Å) positions, thermal parameters set at 1·2 times equivalent isotropic thermal parameter of bonded atoms, not refined. Final discrepancy indices, $R = 0\cdot0410$, $wR = 0\cdot0437$, $R_G = 0\cdot0515$ and GOF $= 1\cdot039$ for 1627 reflections with $F > 2\cdot5\sigma(F)$. Weighting scheme: $w = 1/[\sigma^2(F_o) + 0\cdot00142(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics, $wR = \sum(||F_o| - |F_c||w^{1/2})/\sum(|F_o|w^{1/2})$, $R_G = \{\sum[w(||F_o| - |F_c||)^2]/\sum[w(|F_o|)^2]\}^{1/2}$, 211 parameters refined. Max. $\Delta/\sigma = 0\cdot029$ in final least-squares cycle. Final difference Fourier map showed max. and min. peaks of 0·159 and −0·201 e Å^{-3}. All calculations performed using Data General Eclipse computer with *SHELXTL* programs, which use complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Final atomic parameters are listed in Table 1 and bond lengths and angles in Table 2. The structure is shown in Fig. 1. The absolute configuration at phosphorus is *S*, inferred by reference to the known stereochemistry of (+)-camphor (Oonk, 1965; see also Allen & Rogers, 1971) [and hence (+)-*N*-(trimethylsilyl)camphorimide (2) (Oonk, 1965)]. The correct enantiomorph was fortuitously chosen by the *SHELXTL* program. The imide function deviates significantly from planarity, the N atom lies 0·4163 Å below* the least-squares plane composed of O(1), C(8), C(13) and O(2). The nitrogen itself lies 0·1202 Å below* the C(8), C(13), P plane.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, torsion angles and details of least-squares molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42382 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Defined using the perspective shown in Fig. 1.

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4-Dimethylamino-1-phenyl-1,2,3,5-tetrazin-6-one (I), 5-Dimethylamino-2,3-dihydro-3-oxo-2-*p*-tolylimino-1*H*-1,2,4-triazol-2-ium-1-ide Monohydrate (II) and 1-*o*-Chlorophenylimino-3,5-bis(dimethylamino)-1,2,4-triazolium Tetrafluoroborate (III)

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Abstract. (I): $C_{10}H_{11}N_5O$, $M_r = 217\cdot2$, orthorhombic, *Pbca*, $a = 23\cdot510$ (1), $b = 11\cdot169$ (1), $c = 7\cdot777$ (1) Å, $U = 2042$ (1) Å^3, $Z = 8$, $D_x = 1\cdot413$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 0\cdot828$ mm^{-1}, $F(000) = 912$, $T = 278$ (1) K, $R = 0\cdot050$ for 645 significant reflections. (II): $C_{11}H_{13}N_5O.H_2O$, $M_r = 249\cdot3$, triclinic, $P\bar{1}$, $a = 7\cdot930$ (1), $b = 12\cdot186$ (1), $c = 6\cdot919$ (1) Å, $\alpha =$

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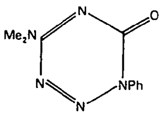
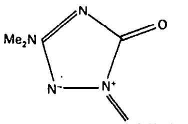
89·088 (2), $\beta = 110·219$ (2), $\gamma = 98·001$ (3)°, $U = 620·9$ (9) Å^3, $Z = 2$, $D_x = 1·333$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 0·806$ mm^{-1}, $F(000) = 264$, $T = 293$ (1) K, $R = 0·057$ for 1402 significant reflections. (III): $C_{12}H_{16}ClN_6^+.BF_4^-$, $M_r = 366·6$, triclinic, $I\bar{1}$, $a = 21·834$ (6), $b = 6·850$ (2), $c = 10·938$ (3) Å, $\alpha = 93·12$ (1), $\beta = 87·76$ (1), $\gamma = 91·94$ (1)°, $U = 1631$ (1) Å^3, $Z = 4$, $D_x = 1·492$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1·54178$ Å, $\mu = 2·417$ mm^{-1}, $F(000) = 752$, $T = 293$ (1) K, $R = 0·084$ for 1718 significant reflections. In (I) the six-membered tetrazinone ring is planar indicating extensive electron delocalization. In (II) the geometry of the five-membered triazolinone ring shows similarities to that found in type *A* mesoionic compounds (*e.g.* the sydnones) {N(2)—C(3) is long [1·546 (5) Å] and the bond angles at C(3) are unequal [105·3 (3), 120·4 (3) and 134·3 (4)°]}; in the cation of (III) these features are less pronounced [1·483 (6) Å and 109·0 (4), 123·6 (4) and 127·4 (5)°, respectively].

Introduction. In the course of our work on 1,2,3,5-tetrazines, we obtained three novel types of compound: 1,2,3,5-tetrazinones, zwitterionic 1,2,3-triazolin-3-ones and 1-arylimino-1,2,4-triazolium salts (Baydar, Boyd, Lindley & Walton, 1985). We now report details of the structure analysis of a member of each class: the phenyltetrazinone (I), the zwitterionic *p*-tolyl derivative (II) and the *o*-chlorophenylimino compound (III).



(I)



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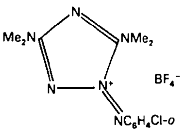

(III)

Experimental. Preparation and physical properties of all three compounds given in Baydar *et al.* (1985). Details of data collection and refinement listed in Table 1. Space-group information and preliminary unit-cell dimensions determined from Weissenberg and precession photographs. Intensity data collected with a Hilger & Watts Y290 diffractometer; Ni-filtered Cu radiation; $\omega/2\theta$ step scans; moving-window estimation of intensity and background (Tickle, 1975). Data for (I) collected at 278 K using crystal coated with epoxy resin due to sublimation of compound in X-ray beam at room temperature. Reference reflections measured every 50 reflections and intensity data scaled to reference data by interpolation. Lp and empirical absorption corrections (North, Phillips & Mathews, 1968) to all data.

Structures solved using direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement of scale factor and positional and anisotropic thermal parameters for nonhydrogen atoms; quantity minimized $\sum w(|F_o| - |F_c|)^2$. For (I) and (II) least-squares routine was a modified version of that originally coded by D. W. J. Cruickshank and J. G. F. Smith; (III) was refined using *SHELX*76 (Sheldrick, 1976). Empirical extinction correction applied for (II) by multiplying uncorrected structure factors, $|F_c'|$, by $(1 + g|F_c'|)^{-1/2}$; for (III) the 020 reflection was omitted since $|F_o| << |F_c|$, a discrepancy also attributed to extinction. H atoms located from difference Fourier syntheses but subsequently fixed in positions with idealized geometry and assumed C—H separation of 1·0 Å; isotropic thermal parameters for all H atoms assigned as 0·10 Å^2. All major computations performed on CDC and Amdahl computers at University of London Computer Centre.

Table 1. *Details of data collection and structure refinement*

	(I)	(II)	(III)
(*a*) Data collection			
Crystal size and shape	0·8 × 0·1 × 0·04 mm	Fragment; max. diameter 0·5 mm	1·0 × 0·3 × 0·1 mm
Scan step size; moving-window parameters	0·02°; 45,30	0·01°; 75,50	0·01°; 90,60
Cell-parameter determination: No.; θ range of reflections	20; 20–30°	20; 20–30°	20; 8–12°
Max. % variation in transmission reflections	6·4	8·8	40·8
Max $(\sin\theta)/\lambda$(Å^{-1})	0·544	0·588	0·544
Range *h*	−25,24	−9,8	−23,23
k	−12,12	−14,14	−7,7
l	−6,8	−5,7	−11,11
Standard reflections No.; variation of intensity sum	4; 4·0%	4; 11·4%	4; 12·6%
No. of intensity measurements	6363	3462	4713
No. of unique reflections	1379	2063	2127
Merging *R* for equivalent *hkl*	0·043	0·020	0·070
No. of unobserved reflections $[I < 3\sigma(I)]$	734	661	408
(*b*) Refinement			
R	0·050	0·057	0·084
wR	0·064	0·063	0·115
Weighting scheme	*	*	†
a	20	20	0·1605
b	20	50	
c	0·001	0·002	
e	0·006	0·005	
$F_{\min}$	10	20	
$(\Delta/\sigma)_{\max}$ in final cycle	0·76	0·08	0·90
Max.; min. heights in final difference Fourier map (e Å^{-3})	0·3; −0·1	0·2; −0·3	0·6; −0·4
Extinction coefficient $g \times 10^5$	—	5·09	—
Scattering factors	Hanson, Herman, Lea & Skillman (1964)		*International Tables for X-ray Crystallography* (1974)

* $w = e$ if $|F_o| < F_{\min}$ else $w = 1 - \exp(-a \sin^2\theta/\lambda^2)/(b + |F_o| + c|F_o|^2)$.
† $w = 1/[(\sigma F_o)^2 + a|F_o|^2]$.

Discussion. Atomic parameters for compounds (I), (II) and (III) are listed in Tables 2(*a*), 2(*b*) and 2(*c*), respectively.* Figs. 1(*a*), 1(*b*) and 1(*c*) are schematic diagrams of the respective molecules, indicating the atomic labelling and the bond lengths and angles, together with their corresponding estimated standard deviations. Figs. 2(*a*), 2(*b*) and 2(*c*) are stereodrawings of molecules (I), (II) and (III), respectively.

In (I) the heterocyclic ring is closely planar, with a maximum displacement out of the least-squares plane of −0·070 (6) Å for N(1). This planarity and the endocyclic bond lengths indicate extensive delocalization of electron density which also extends over N(41) and O(61). However, the N(2)—N(3), C(4)—N(5) and C(6)—O(61) distances, 1·278 (4), 1·313 (6) and 1·213 (6) Å respectively, indicate that the formulation (I) is the dominant canonical form. The phenyl substituent at N(1) is twisted about the N(1)—C(11) bond in order to reduce steric hindrance between O(61) and H(16); the non-bonded separation is 2·713 Å. As a consequence the N(1)—C(11) bond length, 1·440 (5) Å, is as expected for a single bond between sp^2-hybridized C and N atoms; the dihedral angle between the heterocyclic and phenyl-ring planes is 54·0 (2)°.

In the triazolinone (II) the most striking aspect of the molecular geometry is the abnormally long N(2)—C(3) distance of 1·546 (5) Å (*cf.* 1·47 Å for a single bond between sp^3-hybridized C and N atoms). This feature, together with the inequality of the exocyclic bond angles at C(3), is found in several mesoionic compounds of which notable examples are the sydnones (see, for example, Hope & Thiessen, 1969; King, Preston, Suffolk & Turnbull, 1979) and the münchnones (Boyd, Davies, Donaldson, Silver & Wright, 1975). It has been suggested (Hope & Thiessen, 1969) that in compounds of this type the abnormally long endocyclic bond is representative of an incomplete σ bond although conjugation of π orbitals is retained. The entire molecule of (II) is almost perfectly planar, indicating extensive electron delocalization; the maximum deviation out of the least-squares plane is −0·028 (6) Å for the tolyl methyl C atom, C(28). Steric hindrance between N(1) and H(27) (non-bonded separation 2·203 Å) is minimized by the opening out of the angles N(1)—N(2)—N(21) and N(21)—C(22)—C(27) to 130·5 (3) and 128·5 (3)° respectively.

In (III), the geometry of the triazolium cation is similar in many respects to the triazolinone molecule (II). Thus the cation is essentially planar with a maximum out-of-plane displacement of −0·032 (7) Å for the dimethylamino C atom C(32). Steric hindrance between N(2) and H(16) (non-bonded separation 2·205 Å) is minimized by angles of 130·6 (5)° for N(2)—N(1)—N(11) and 127·8 (4)° for N(11)—C(11)—C(16). Within the heterocyclic ring the N(1)—C(5) separation, 1·483 (6) Å, is again abnormally long but shorter than the corresponding bond in (II); the difference in the exocyclic angles at C(5) is also less pronounced. Further, the N(4)—C(5) and N(1)—N(2)

Table 2. *Fractional coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *for non-hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}(\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
(*a*) Compound (I)				
N(1)	0·3715 (1)	0·3799 (3)	0·4335 (4)	38 (1)
N(2)	0·3906 (1)	0·4799 (3)	0·3585 (5)	43 (1)
N(3)	0·4428 (1)	0·4885 (3)	0·3143 (5)	44 (1)
C(4)	0·4777 (2)	0·3889 (4)	0·3477 (5)	39 (1)
N(41)	0·5308 (1)	0·3990 (3)	0·2874 (5)	45 (1)
C(42)	0·5701 (2)	0·2996 (4)	0·3130 (7)	59 (2)
C(43)	0·5510 (2)	0·5011 (4)	0·1871 (6)	54 (2)
N(5)	0·4627 (1)	0·2935 (3)	0·4352 (5)	47 (1)
C(6)	0·4074 (2)	0·2838 (4)	0·4828 (5)	43 (1)
O(61)	0·3876 (1)	0·2008 (3)	0·5637 (5)	64 (1)
C(11)	0·3112 (2)	0·3789 (4)	0·4661 (5)	40 (1)
C(12)	0·2867 (2)	0·4734 (4)	0·5500 (6)	46 (1)
C(13)	0·2275 (2)	0·4758 (4)	0·5733 (6)	56 (2)
C(14)	0·1950 (2)	0·3823 (4)	0·5132 (6)	53 (2)
C(15)	0·2201 (2)	0·2884 (4)	0·4291 (6)	53 (2)
C(16)	0·2792 (2)	0·2847 (4)	0·4045 (6)	47 (2)
(*b*) Compound (II)				
N(1)	0·6428 (3)	0·6091 (2)	0·7676 (4)	39 (1)
N(2)	0·4689 (3)	0·6234 (2)	0·7000 (4)	40 (1)
C(3)	0·4537 (5)	0·7472 (3)	0·6574 (6)	46 (2)
O(31)	0·3076 (3)	0·7782 (2)	0·5949 (5)	71 (2)
N(4)	0·6233 (4)	0·7971 (2)	0·7055 (4)	44 (1)
C(5)	0·7273 (4)	0·7153 (2)	0·7663 (5)	37 (1)
N(51)	0·9056 (3)	0·7336 (2)	0·8260 (4)	45 (1)
C(52)	1·0150 (5)	0·6440 (3)	0·8937 (7)	60 (2)
C(53)	1·0053 (5)	0·8448 (3)	0·8312 (7)	57 (2)
N(21)	0·3264 (3)	0·5541 (2)	0·6708 (4)	36 (1)
C(22)	0·3339 (4)	0·4415 (3)	0·7088 (5)	41 (1)
C(23)	0·1615 (4)	0·3791 (3)	0·6673 (6)	50 (2)
C(24)	0·1434 (5)	0·2673 (3)	0·6941 (6)	51 (2)
C(25)	0·2944 (5)	0·2115 (3)	0·7645 (5)	47 (2)
C(26)	0·4651 (5)	0·2738 (3)	0·8074 (6)	51 (2)
C(27)	0·4877 (4)	0·3868 (3)	0·7817 (5)	46 (2)
C(28)	0·2735 (6)	0·0882 (3)	0·7901 (7)	68 (2)
O(*W*)	0·2903 (6)	0·9526 (3)	0·2952 (6)	120 (2)
(*c*) Compound (III)				
Cl(1)	−0·0316 (1)	0·2575 (2)	0·2111 (1)	79 (1)
N(1)	0·0527 (2)	0·2369 (5)	0·5379 (3)	51 (1)
N(11)	0·0189 (2)	0·2436 (5)	0·4464 (4)	56 (1)
C(11)	−0·0434 (2)	0·2626 (6)	0·4582 (4)	54 (2)
C(12)	−0·0732 (3)	0·2699 (7)	0·3466 (5)	59 (2)
C(13)	−0·1364 (3)	0·2890 (7)	0·3435 (5)	69 (2)
C(14)	−0·1712 (3)	0·3025 (8)	0·4486 (6)	78 (2)
C(15)	−0·1434 (3)	0·2899 (7)	0·5606 (5)	72 (2)
C(16)	−0·0805 (2)	0·2725 (6)	0·5679 (4)	60 (2)
N(2)	0·0387 (2)	0·2417 (5)	0·6539 (3)	54 (1)
C(3)	0·0950 (2)	0·2312 (6)	0·7066 (5)	61 (2)
N(31)	0·1004 (2)	0·2283 (6)	0·8262 (4)	69 (2)
C(31)	0·1616 (3)	0·2122 (10)	0·8789 (6)	86 (2)
C(32)	0·0482 (3)	0·2495 (9)	0·9096 (6)	81 (2)
N(4)	0·1436 (2)	0·2125 (5)	0·6249 (4)	58 (1)
C(5)	0·1199 (2)	0·2162 (6)	0·5203 (5)	57 (2)
N(51)	0·1487 (2)	0·2026 (6)	0·4109 (4)	69 (2)
C(51)	0·2166 (3)	0·1838 (11)	0·4096 (6)	88 (2)
C(52)	0·1227 (3)	0·2089 (11)	0·2897 (6)	90 (3)
B(1)	0·1549 (3)	0·7377 (9)	0·0728 (6)	63 (2)
F(1)	0·1726 (2)	0·7062 (7)	0·0465 (3)	110 (2)
F(2)	0·1987 (2)	0·8572 (9)	0·1296 (5)	132 (2)
F(3)	0·1029 (2)	0·8414 (12)	0·0778 (7)	169 (3)
F(4)	0·1477 (6)	0·5728 (8)	0·1234 (6)	235 (6)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and bond distances and angles for the BF_4^- anion of (III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42346 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances, 1·276 (7) and 1·292 (5) Å, show more double-bond character in the cation of (III) than the corresponding distances in (II) [C(3)—N(4) 1·326 (5) and N(1)—N(2) 1·330 (3) Å].

In the crystal structures of compounds (I), (II) and (III) there are no non-bonded distances significantly shorter than the sums of the respective van der Waals radii. Compound (II) contains a molecule of water of crystallization which hydrogen bonds to O(31) at an interoxygen distance of 2·925 (5) Å. Bond lengths and angles for the BF_4^- anion of (III) have been deposited.

We thank the SERC for financial support.

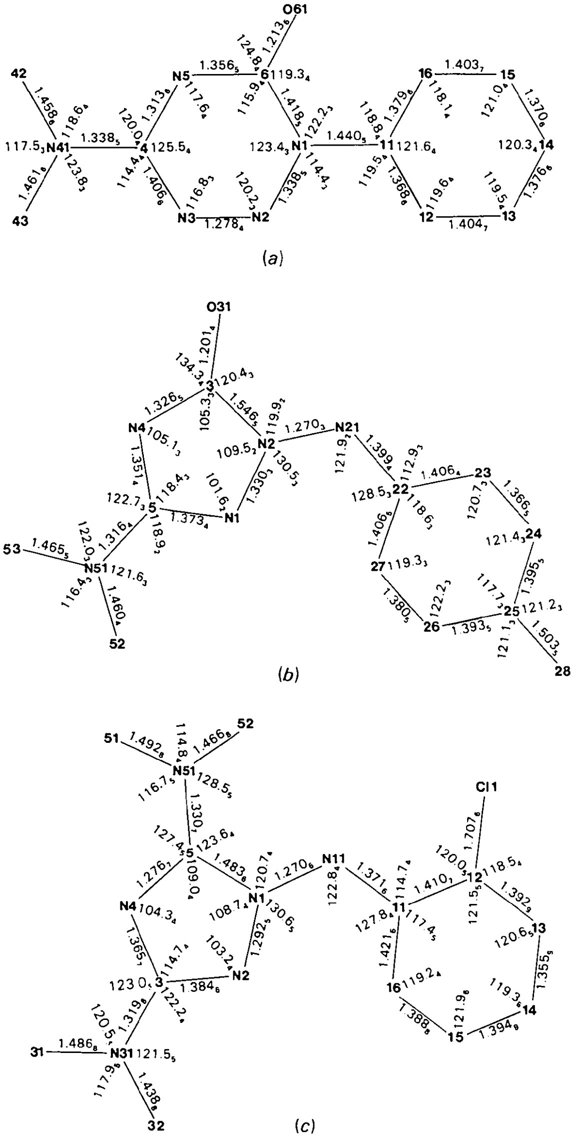

Fig. 1. Schematic drawings showing the atom labelling and intramolecular bond lengths (Å) and angles (°) with e.s.d.'s given as subscripts. (*a*) Compound (I), (*b*) compound (II), (*c*) compound (III).

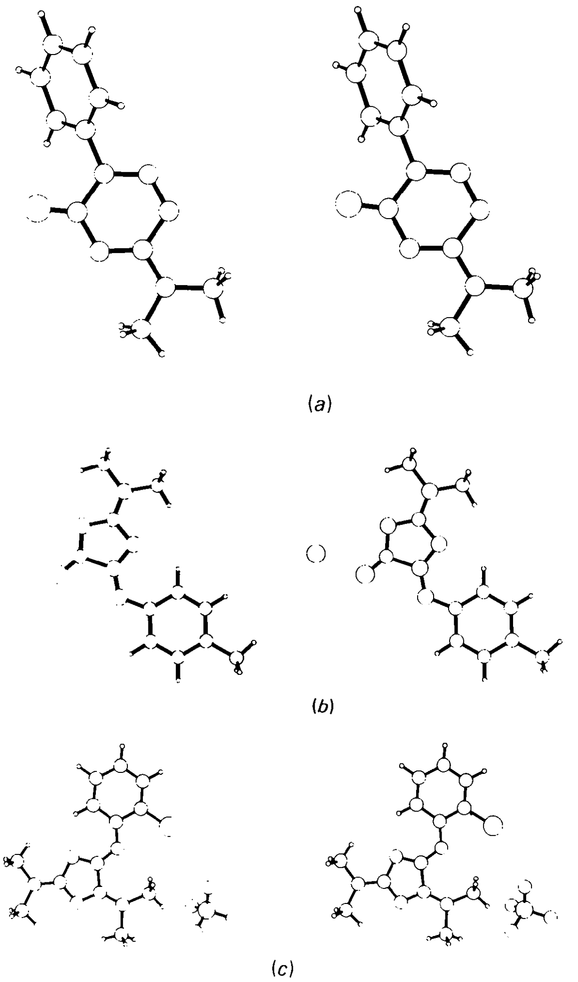

Fig. 2. Stereodrawings of molecules of (*a*) (I), (*b*) (II) and (*c*) (III).

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