an NCS^- anion in (1) or (2), that is, the BF_4^- anion forms a hydrogen bond with thiazolium C(2)H and it further contacts electrostatically with the pyrimidine ring.* Analogously to the above-mentioned NCS^- anion bridge in (1) and (2), there is a water bridge between the pyrimidine and the thiazolium rings in (2) and (3), that is, a water molecule, O(*WB*) in (2) or O(*W*) in (3), forms a hydrogen bond with N(4′α)H and also takes part in an electrostatic interaction with the thiazolium ring [*B* molecule for (2); not shown in Fig. 1(*b*)].* This type of water bridge has often been observed in other hydrated thiamine structures with the *F* conformation, *e.g.* thiamine.-Cl.H_2O (Pletcher, Sax, Sengupta, Chu & Yoo, 1972), thiamine.picrolonate.$2H_2O$ (Shin, Pletcher, Blank & Sax, 1977), thiaminepyrophosphate.$4{\cdot}5H_2O$ (Pletcher, Blank, Wood & Sax, 1979), thiamine.PF_6.H_2O (Aoki, Yamazaki, Waragai & Itokawa, 1988), thiaminium.$(PF_6)_2$.$4H_2O$ (Aoki *et al.*, 1988) and thiamine monophosphate.PF_6.$2H_2O$ (Aoki *et al.*, 1988). This suggests that the water bridge stabilizes the *F* conformation of thiamine.

A base–base pairing through a pair of N(4′α)—H···N(3′) hydrogen bonds forms across a centre of symmetry in (1) (not shown in Fig. 1*a*) and between molecules *A* and *B* in (2), while it does not in (3). An O(5γ)—H···N(1′) hydrogen bond, which is commonly formed in (1)–(3), creates a thiamine–thiamine self-dimer in (1) and (2), each across a centre of symmetry [*i.e.* between *A* and *A* and between *B* and *B* molecules in (2)] while it creates a polymeric molecular array of thiamines in (3).

In summary, this work presents additional examples showing the thiamine–anion complexation, where an anion molecule forms a hydrogen bond with the acidic C(2)H and it further interacts electrostatically with the pyrimidine ring of the same thiamine molecule with the *F* conformation, thus serving as a model for the substrate anion fixation near the catalytic C(2) site in the enzyme system.

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* See deposition footnote.

Acta Cryst. (1990). C**46**, 1487–1490

Structure of 3,5-Bis(dimethylamino)-6-phenyl-1,2,4-triazine 1-Imide

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(*Received* 11 *October* 1989; *accepted* 22 *November* 1989)

Abstract. $C_{13}H_{18}N_6$, $M_r = 258{\cdot}32$, orthorhombic, $P2_12_12$, $a = 15{\cdot}095\,(3)$, $b = 16{\cdot}333\,(3)$, $c = 5{\cdot}643\,(1)$ Å, $V = 1391{\cdot}3\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}233$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}56$ mm^{-1}, $F(000) = 552$, $T = 293\,(1)$ K, final $R = 0{\cdot}042$, $wR = 0{\cdot}046$ for 2500 independent reflections. The 1,2,4 triazide ring is not strictly planar, the phenyl ring makes an angle of $-63{\cdot}5\,(1)°$ with the plane through N1, N2, C5, N11. The bond distances in the triazinium imide, particularly the N1—N11 (imide) at 1·296 (2) Å, indicate that canonical forms involving an exocyclic N—N double bond at N1

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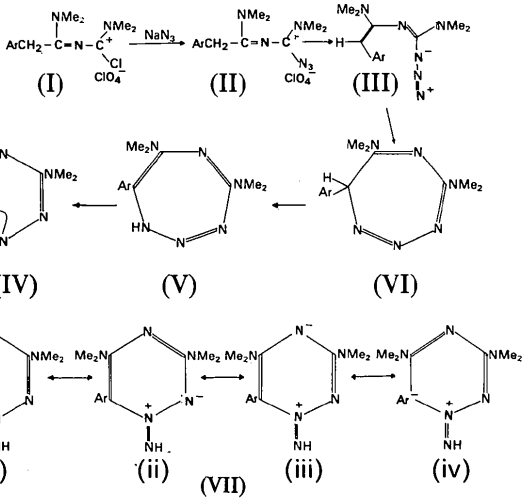
make important contributions to the overall resonance hybrid. The crystal structure contains intermolecular H bonds involving the imide H atom.

Introduction. We report here the first representatives of the 1,2,4-triazine 1-imide system. These compounds (VII) were obtained by reaction of the azabutenylium salts (I) (Boyd, Lindley & Nicolaou, 1984) with sodium azide and treatment of the resulting azido perchlorates (II) with sodium hydroxide. Contrary to our earlier suggestion (Boyd, Lindley, Mitchell & Nicolaou, 1985), we now consider that the products are formed by 1,7-dipolar cyclization of the azides (III) to tetrazepines (IV), which rearrange *via* the tautomers (V) and the bicyclic compounds (VI), as shown in the reaction scheme. The appearance of a blue colour may be due to the tetrazepines (IV) or (V) and there are precedents for the last two steps in the sequence in the chemistry of pyridine *N*-imides, (Timpe, 1974) and benzocinnoline *N*-imide (Gait, Rees & Storr, 1971). The triazinium imides are stable pale-yellow solids; they are noteworthy because, like benzocinnoline *N*-imide, they lack an electron-withdrawing substituent on the exocyclic N atom, a feature common to all stable heterocyclic *N*-imides (Timpe, 1974).



(VII*a*): Ar = Ph; (VII*b*): Ar = *p*-MeC_6H_4; (VII*c*): Ar = *p*-$MeOC_6H_4$; (VII*d*): Ar = *p*-ClC_6H_4.

Experimental. A solution of sodium azide (2·2 g, 1·1 mol equiv.) in water (4 ml) was added dropwise to a magnetically stirred solution of 1-chloro-1,3-bis(dimethylamino)-4-phenylbut-2-ene-1-ylium perchlorate (I) (10·0 g) in acetonitrile (40 ml). The mixture was stirred for 1 h, filtered and evaporated *in vacuo*. The residue was recrystallized from acetonitrile/ethyl acetate, yielding 1-azido-1,3-bis(dimethylamino)-4-phenylbut-2-en-1-ylium perchlorate (II*a*) (9·12 g, 90%), m.p. 394 K (decomp.), ν_{max} 2140 (N_3), 1640 (C=N) and 1100 (*br*) (ClO_4) cm^{-1}, δ($CDCl_3$) 7·44–7·26 (*br s*, 5H, Ph), 4·1 (*s*, 2H, CH), 3·47 (*s*, 3H, Me), 3·39 (*s*, 3H, Me), 3·01 (*s*, 3H, Me) and 2·96 (*s*, 3H, Me). Found: C 43·4, H 5·25, N 23·6%; $C_{13}H_{19}ClN_6O_4$ requires C 43·5, H 5·35, N 23·4%. A stirred solution of this azido perchlorate (5·0 g) in acetonitrile (20 ml) was slowly treated with 2*M* aqueous sodium hydroxide (14 ml, 2·0 mol equiv.). A deep-blue colour was produced which quickly faded. The mixture was stirred for 30 min, water (20 ml) was added and the mixture was extracted with ethyl acetate (3 × 15 ml). The combined extracts were dried ($MgSO_4$) and evaporated *in vacuo* leaving pale-yellow 3,5-bis(dimethylamino)-6-phenyl-1,2,4-triazine 1-imide (VII*a*) (2·8 g, 78%), m.p. 383 K (decomp.) from ethanol, ν_{max} 3240 (NH) and 1600 cm^{-1}, δ($CDCl_3$) 8·1 (*br s*, 1H, NH), 7·46 (*br s*, 5H, Ph), 3·1 (*s*, 6H, NMe_2) and 2·7 (*s*, 6H, NMe_2). Found: C 60·6, H 7·1, N 33·0%; $C_{13}H_{18}N_6$ requires C 60·45, H 7·05, N 32·5%. The other compounds, (VII*b*–*d*) having similar spectral characteristics, were prepared in an analogous manner.*

Intensity data were collected from a prismatic crystal, 0·25 × 0·50 × 0·75 mm, with a Hilger and Watts *Y*290 four-circle diffractometer (Ni-filtered Cu $K\alpha$ radiation). Unit-cell parameters and their e.s.d.'s were derived from 20 reflections with $25·3 < \theta < 29·7°$. Intensity measurements were made for 4445 reflections ($h \pm 18$, $k \pm 19$, $-4 < l < 6$; $2\theta_{max} = 140°$) in the $\omega/2\theta$ scan mode with $\Delta\omega = (0·75 + 0·142\tan\theta)°$ and 0·01° steps at 1 s per step; stationary background counts were taken for one-tenth of the total scan time either side of each peak. Four reference reflections (442, $\bar{4}\bar{4}2$, $4\bar{2}2$, $\bar{4}2\bar{2}$; typical r.m.s.d. = 2·0%) were measured every 50 measurements; no significant crystal decay was observed. The intensity data were corrected for Lp and absorption, (North, Phillips & Mathews, 1968), using the 00*l* ($l = 1 - 3$) reflections; maximum and minimum normalized transmission factors 1·06 and 1·00, respectively. Reflections were merged (R_{int} = 0·025) to yield 2500 reflections with $I > 3\sigma(I)$.

The structure was solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *F*'s with *SHELX*76 (Sheldrick, 1976). Initially all non-H atoms were treated isotropically to give $R = 0·118$; the phenyl H atoms, imide H atom, and some of the methyl H atoms were located from a difference Fourier synthesis as diffuse electron-density maxima,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes for (VII*a*) and analytical details for (VII*b*–*d*) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52800 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

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

	x	y	z	U_{eq}(Å^2)
N1	0·3859 (1)	0·0752 (1)	0·3754 (3)	0·045 (1)
N11	0·3816 (1)	−0·0021 (1)	0·4260 (4)	0·060 (1)
N2	0·4484 (1)	0·0988 (1)	0·2148 (3)	0·050 (1)
C3	0·4444 (1)	0·1772 (1)	0·1496 (4)	0·048 (1)
N31	0·4982 (1)	0·1979 (1)	−0·0333 (3)	0·067 (1)
C32	0·5034 (2)	0·2805 (2)	−0·1194 (5)	0·079 (1)
C33	0·5503 (2)	0·1371 (2)	−0·1562 (5)	0·074 (1)
N4	0·3945 (1)	0·2363 (1)	0·2457 (1)	0·053 (1)
C5	0·3382 (1)	0·2128 (1)	0·4160 (4)	0·030 (1)
N51	0·2902 (1)	0·2740 (1)	0·5143 (3)	0·058 (1)
C52	0·2501 (2)	0·2710 (2)	0·7480 (5)	0·074 (1)
C53	0·2978 (2)	0·3565 (1)	0·4180 (5)	0·078 (1)
C6	0·3279 (1)	0·1298 (1)	0·4795 (4)	0·044 (1)
C61	0·2580 (1)	0·0938 (1)	0·6295 (4)	0·046 (1)
C62	0·2776 (1)	0·0532 (1)	0·8406 (4)	0·051 (1)
C63	0·2113 (2)	0·0228 (1)	0·9821 (4)	0·063 (1)
C64	0·1243 (2)	0·0302 (2)	0·9163 (5)	0·075 (1)
C65	0·1031 (1)	0·0683 (2)	0·7061 (5)	0·074 (1)
C66	0·1694 (1)	0·1004 (1)	0·5622 (4)	0·060 (1)

Table 2. *Bond distances* (Å) *and bond angles* (°) *for the non-*H *atoms; e.s.d.'s include cell-parameter errors*

N1—N11	1·296 (2)	C5—C6	1·411 (2)
N1—N2	1·364 (3)	N51—C52	1·452 (3)
N1—C6	1·381 (3)	N51—C53	1·457 (3)
N2—C3	1·334 (2)	C6—C61	1·475 (3)
C3—N31	1·356 (3)	C61—C62	1·395 (3)
C3—N4	1·339 (3)	C61—C66	1·394 (2)
N31—C32	1·436 (4)	C62—C63	1·373 (3)
N31—C33	1·444 (4)	C63—C64	1·370 (4)
N4—C5	1·339 (2)	C64—C65	1·377 (4)
C5—N51	1·353 (3)	C65—C66	1·391 (3)
N11—N1—N2	117.2 (2)	C5—N51—C52	124.8 (2)
N11—N1—C6	120.2 (2)	C5—N51—C53	119.2 (2)
N2—N1—C6	122.6 (2)	C52—N51—C53	113.7 (2)
N1—N2—C3	115.0 (2)	N1—C6—C5	116.3 (2)
N2—C3—N31	115.0 (2)	N1—C6—C61	116.1 (2)
N2—C3—N4	127.3 (2)	C5—C6—C61	127.4 (2)
N31—C3—N4	117.7 (2)	C6—C61—C62	121.9 (2)
C3—N31—C32	121.6 (2)	C6—C61—C66	119.9 (2)
C3—N31—C33	121.3 (2)	C62—C61—C66	118.2 (2)
C32—N31—C33	117.0 (2)	C61—C62—C63	120.9 (2)
C3—N4—C5	116.2 (2)	C62—C63—C64	120.6 (2)
N4—C5—N51	115.0 (2)	C63—C64—C65	119.7 (2)
N4—C5—C6	121.8 (2)	C64—C65—C66	120.4 (2)
N51—C5—C6	123.1 (2)	C61—C66—C65	120.1 (2)

0·4–0·6 e Å^{-3}. In the subsequent refinement the H atoms bonded to C atoms were placed in fixed positions assuming idealized geometry and C—H distances of 1·0 Å, but the H atom at N11 was fixed at the appropriate electron-density maximum; all the non-H atoms were permitted to refine anisotropically. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ and convergence was reached at $R = 0·042$ [wR = 0·045, 245 parameters, $w^{-1} = \sigma^2(F) + 0·000002|F|^2$, $(\Delta/\sigma)_{\max} = 0·68$]. The final difference Fourier synthesis showed no residual densities outside the range $-0·26$ to 0·32 e Å^{-3}. The crystal appeared to exhibit some extinction for which the F_c values were corrected by refinement of an impirical isotropic extinction parameter, X [$= 0·35\,(3) \times 10^{-5}$]; $F_c' = F_c[1 - (XF_c^2/\sin\theta)]$. Scattering factors were taken from Cromer & Mann (1968). Molecular geometry calculations were performed using programs written by Lindley (unpublished).

Discussion. Refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1,* and bond lengths and bond angles for the non-H atoms are listed in Table 2. Fig. 1 is a stereo drawing of the molecule viewed parallel to the *c* axis; the atomic numbering scheme is implicit in the compound name.

The 1,2,4-triazide ring is not strictly planar and the dihedral angle between the planes through atoms N1, N2, C6 and N11, and C3, N4 and C5 is 4·65 (6)°. The phenyl ring at C6 is inclined at a dihedral angle of −63·5 (1)° to the plane through N1, N2, C5 and N11. The structure determination shows that the molecule is not satisfactorily represented by formula VII(i), in which the positively charged aromatic triazinium ring is linked to the exocyclic negatively charged N atom by a single bond, as in pyridine 1-nitroimide, which possesses a long N—N bond, 1·421 Å, emanating from the pyridine ring, and whose C—N bonds (1·340 and 1·350 Å) and C—C

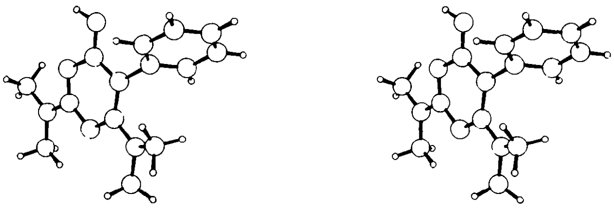

Fig. 1. A stereo drawing (Motherwell, 1978) of the molecule of 2,5-bis(dimethylamino)-6-phenyl-1,2,4-triazine 1-imide, $C_{13}N_{18}N_6$; the atomic labelling is implicit in the compound name.

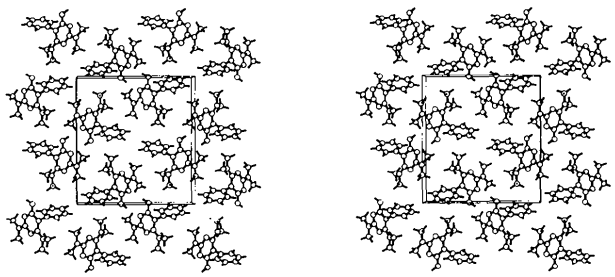

Fig. 2. The crystal packing viewed along the unit-cell *c* axis. Intermolecular H bonds are formed between N11 of one molecule and N2 of a second related by the twofold symmetry operation ($1 - x$, $-y$, z); the N···N distance is 3·240 (2) Å. (H bonds are omitted for clarity.)

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* See deposition footnote

bonds (1·366 to 1·387 Å) are intermediate between single and double bonds (Arriau, Deschamps, Duke, Epsztajn, Katritzky, Lunt, Mitchell, Rizvi & Roch, 1974). The bond distances in the triazinium imide indicate that, on the contrary, the canonical forms (i)–(iv) of (VII*a*) make important contributions to the resonance hybrid, due, presumably, to the presence of the electronegative N atoms at positions 2 and 4.

The molecular packing is shown in Fig. 2 viewed along the unit-cell *c* axis, Intermolecular H bonds are formed between the 1-imide N atom, N11, and N2 of a molecule related by the twofold symmetry operation $(1-x, \ -y, \ z)$; the N···N separation is 3·240 (2) Å. This type of intermolecular interaction presumably assists in stabilizing the 1-imide structure in the crystal. There are no other non-bonded contacts which are significantly closer than the sum of the corresponding van der Waals radii.

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Acta Cryst. (1990). **C46**, 1490–1492

Structure of Stearic Acid *E* Form

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(*Received* 7 *September* 1989; *accepted* 13 *November* 1989)

Abstract. *E* form of octadecanoic acid, $C_{18}H_{36}O_2$, $M_r = 284{\cdot}48$, monoclinic, $P2_1/a$, $a = 5{\cdot}603$ (1), $b = 7{\cdot}360$ (1), $c = 50{\cdot}789$ (9) Å, $\beta = 119{\cdot}40$ (2)°, $V = 1824{\cdot}6$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}04$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 5{\cdot}0$ cm^{-1}, $F(000) = 640$, $T = 283$ K, $R(F) = 0{\cdot}052$, $wR(F) = 0{\cdot}082$ for 2225 unique observed reflections with $F > 3\sigma(F)$. The polymethylene chain of the acyl group takes an all-*trans* conformation and forms an $O\perp$ type subcell with $a_s = 7{\cdot}36$, $b_s = 5{\cdot}02$, and $c_s = 2{\cdot}55$ Å. The a_s axis is parallel to the unique axis (*b* axis) and the c_s axis is tilted by about 26° from the normal of the basal plane toward the *a* axis.

Introduction. It is well known that even-numbered *n*-fatty acids crystallize into various modifications depending on the crystallization conditions. Holland & Nielson (1962) obtained single crystals of stearic acid (octadecanoic acid) from a diethyl ether solution. The crystal had a lozenge shape with an acute interedge angle of about 74° like the *B* form but showed an infrared spectrum different from those of any of the previously known modifications (*A*, *B* and *C* forms). They concluded that the crystal was of a new modification, and named it the *E* form. Based on the investigation of the infrared spectra and on the morphological observation, they derived the crystal structure of the *E* form as follows (Holland & Nielson, 1963):

(1) Molecules formed an *o*-PE type ($O\perp$) sublattice in the unit cell that belongs to a monoclinic system as in the *B* and *C* forms.

(2) The polymethylene chain took the all-*trans* conformation as in the *C* form and was inclined toward the basal plane in the same manner (the direction and the angle of inclination) as in the *B* form.

Except for the work carried out by Kobayashi, Kobayashi, Cho & Kaneko (1986) who came to the same conclusions through Raman spectroscopy,

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