

- GOUBITZ, K., REISS, C. A. & HEIJENRIJK, D. (1989a). *Acta Cryst.* C45, 1356–1358.
- GOUBITZ, K., REISS, C. A. & HEIJENRIJK, D. (1989b). *Acta Cryst.* C45, 1364–1366.
- GOUBITZ, K., REISS, C. A., HEIJENRIJK, D., JONKER, S. A. & VERHOEVEN, J. W. (1989). *Acta Cryst.* C45, 1348–1350.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* 17, 781–782.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* B25, 1750–1752.
- KRONENBURG, M. J., GOUBITZ, K., REISS, C. A. & HEIJENRIJK, D. (1989). *Acta Cryst.* C45, 1352–1353.
- KRONENBURG, M. J., REISS, C. A., GOUBITZ, K. & HEIJENRIJK, D. (1989). *Acta Cryst.* C45, 1361–1363.
- REISS, C. A., GOUBITZ, K. & HEIJENRIJK, D. (1989a). *Acta Cryst.* C45, 1350–1352.
- REISS, C. A., GOUBITZ, K. & HEIJENRIJK, D. (1989b). *Acta Cryst.* C45, 1354–1356.
- REISS, C. A., GOUBITZ, K., ZOUTBERG, M. C. & HEIJENRIJK, D. (1989). *Acta Cryst.* C45, 1366–1369.
- ROSZAK, A. & BOROWIAK, T. (1987). *Acta Cryst.* C43, 498–501.
- ROSZAK, A. & DUAX, W. L. (1987). *Acta Cryst.* C43, 251–254.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
- ZOUTBERG, M. C., REISS, C. A., GOUBITZ, K. & HEIJENRIJK, D. (1989). *Acta Cryst.* C45, 1359–1361.

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Structure of *trans*-Bis(4-dimethylaminonaphthalene-1-azo)-4,4'-stilbene

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Abstract. $C_{38}H_{34}N_6$, $M_r = 574.73$, monoclinic, $P2_1/c$, $a = 9.286$ (1), $b = 9.375$ (1), $c = 35.250$ (4) Å, $\beta = 92.681$ (5)°, $V = 3065.4$ (3) Å³, $Z = 4$, $D_m = 1.25$ (2), $D_x = 1.245$ (1) Mg m⁻³, $Cu K\alpha$, $\lambda = 1.54178$ Å, $\mu = 0.508$ mm⁻¹, $F(000) = 1216$, $T = 298$ K, $R = 0.053$, 3819 unique observed reflections. All distances and angles lie within the range of values found for compounds having a similar composition to that of the title compound. The molecule can be described as quasi centrosymmetric and nearly planar. Intermolecular bonding is by van der Waals interaction.

Introduction. Azo and anthraquinone derivatives are the most frequently used dyes for liquid crystalline guest–host systems. The azo compounds show in most cases a sufficient solubility and have higher order parameters and greater extinction coefficients than the anthraquinone dyes. A serious problem in their use is the poor stability to illumination due to *cis*–*trans* isomerization in liquid crystalline solution. New azo derivatives with a more extended molecular shape have been developed that have significantly higher stabilities (Seki, Shishido, Uchida & Wada, 1982).

Experimental. The title compound was synthesized using 4,4'-diaminostilbene dihydrochloride and 1-dimethylaminonaphthalene (Aftergut & Cole, 1979). There resulted a mixture of more than ten different dyes and so column chromatography was used for purification of the main product which was additionally characterized by VIS, NMR, and mass spectroscopy, yield about 60%. Reddish brown crystals in the form of sheets could be obtained by slow evaporation of a solution with chloroform. The main problem with the structure analysis was the availability of single crystals, because by recrystallization from different solvents twins were nearly always obtained. The crystal density was determined using a pycnometer. A crystal of size $0.04 \times 0.35 \times 1.4$ mm with well developed faces (001), (010) and (10 $\bar{1}$) was used for the X-ray measurements with a Stoe Stadi IV diffractometer with graphite monochromator. Lattice parameters were obtained by least-squares fit of 50 reflections, $25 \leq 2\theta \leq 62^\circ$; intensity data were collected using ω – 2θ scan, absorption was ignored ($\mu R = 0.102$); max. $\sin\theta/\lambda = 0.58$ Å⁻¹; h : $-10 \rightarrow 10$, k : $0 \rightarrow 10$, l : $0 \rightarrow 39$; three standard reflections measured after every 50 reflections showed no significant intensity variations. 4878 reflections were measured of which 4203 were unique and 3819 with $F_o > 2\sigma(F_o)$ were subsequently used in the refinement ($R_{int} = 0.0386$). The structure was solved by the direct methods; F magnitudes were used in full-matrix least-squares refinement; all atoms (H atoms inclu-

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Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) of non-H atoms, with e.s.d.'s in parentheses

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

	x	y	z	U_{eq}
N(1)	742 (2)	3283 (2)	912 (1)	62 (1)
N(2)	6369 (2)	4162 (2)	1535 (1)	66 (1)
N(3)	6806 (2)	3295 (2)	1786 (1)	73 (1)
N(4)	18818 (2)	3874 (2)	3337 (1)	69 (1)
N(5)	19094 (2)	3261 (2)	3649 (1)	62 (1)
N(6)	24394 (2)	4924 (2)	4363 (1)	70 (1)
C(1)	4947 (2)	3904 (2)	1386 (1)	58 (1)
C(2)	4000 (2)	3000 (2)	1554 (1)	66 (1)
C(3)	2608 (2)	2802 (2)	1399 (1)	65 (1)
C(4)	2131 (2)	3480 (2)	1070 (1)	53 (1)
C(5)	3133 (2)	4361 (2)	0874 (1)	52 (1)
C(6)	2818 (2)	4906 (2)	0506 (1)	61 (1)
C(7)	3776 (2)	5739 (2)	0327 (1)	71 (1)
C(8)	5102 (3)	6077 (3)	0507 (1)	73 (2)
C(9)	5475 (2)	5524 (2)	0852 (1)	67 (1)
C(10)	4529 (2)	4618 (2)	1045 (1)	55 (1)
C(11)	-68 (3)	2057 (3)	1043 (1)	82 (2)
C(12)	-178 (3)	4506 (3)	0832 (1)	79 (2)
C(13)	8224 (2)	3569 (2)	1937 (1)	65 (1)
C(14)	9055 (3)	4758 (2)	1856 (1)	67 (1)
C(15)	10441 (3)	4866 (3)	2011 (1)	67 (1)
C(16)	11040 (2)	3837 (2)	2253 (1)	61 (1)
C(17)	10181 (3)	2669 (3)	2334 (1)	76 (2)
C(18)	8807 (3)	2536 (3)	2177 (1)	80 (2)
C(19)	12512 (2)	3998 (2)	2411 (1)	64 (1)
C(20)	13192 (2)	3162 (2)	2665 (1)	64 (1)
C(21)	14657 (2)	3323 (2)	2827 (1)	59 (1)
C(22)	15145 (2)	2401 (2)	3115 (1)	66 (1)
C(23)	16502 (2)	2528 (2)	3288 (1)	66 (1)
C(24)	17417 (2)	3594 (2)	3175 (1)	60 (1)
C(25)	16954 (3)	4495 (3)	2883 (1)	79 (2)
C(26)	15605 (3)	4375 (3)	2714 (1)	76 (2)
C(27)	20491 (2)	3577 (2)	3810 (1)	55 (1)
C(28)	21630 (2)	3974 (2)	3602 (1)	67 (1)
C(29)	22943 (2)	4378 (3)	3781 (1)	68 (1)
C(30)	23121 (2)	4421 (2)	4167 (1)	59 (1)
C(31)	21980 (2)	3917 (2)	4395 (1)	54 (1)
C(32)	22141 (3)	3802 (2)	4792 (1)	65 (1)
C(33)	21046 (3)	3327 (3)	5002 (1)	75 (2)
C(34)	19718 (3)	2969 (3)	4825 (1)	72 (2)
C(35)	19515 (2)	3047 (2)	4443 (1)	62 (1)
C(36)	20646 (2)	3498 (2)	4213 (1)	53 (1)
C(37)	25709 (3)	4841 (4)	4153 (1)	95 (2)
C(38)	24221 (8)	6323 (3)	4534 (1)	103 (2)

Table 2. Selected intramolecular interatomic distances (\AA) and angles ($^\circ$)

N(1)—C(4)	1.393 (2)	C(21)—C(22)	1.394 (3)
N(1)—C(11)	1.460 (3)	C(21)—C(26)	1.394 (3)
N(1)—C(12)	1.449 (3)	C(23)—C(24)	1.382 (3)
N(2)—N(3)	1.256 (3)	C(24)—C(25)	1.383 (3)
C(1)—N(2)	1.418 (3)	N(4)—N(5)	1.256 (2)
N(3)—C(13)	1.420 (3)	N(4)—C(24)	1.421 (3)
C(1)—C(2)	1.375 (3)	N(5)—C(27)	1.422 (3)
C(1)—C(10)	1.415 (3)	C(27)—C(28)	1.367 (3)
C(13)—C(14)	1.393 (3)	C(27)—C(36)	1.422 (3)
C(13)—C(18)	1.380 (3)	C(29)—C(30)	1.364 (3)
C(15)—C(16)	1.389 (3)	C(30)—C(31)	1.437 (3)
C(16)—C(17)	1.392 (3)	N(6)—C(37)	1.421 (3)
C(16)—C(19)	1.458 (3)	N(6)—C(38)	1.460 (3)
C(19)—C(20)	1.328 (3)		1.456 (4)
C(20)—C(21)	1.458 (3)		
C(11)—N(1)—C(4)	117.3 (2)	C(26)—C(21)—C(20)	123.5 (2)
C(12)—N(1)—C(4)	119.9 (2)	C(26)—C(21)—C(22)	117.3 (2)
C(12)—N(1)—C(11)	112.1 (2)	C(23)—C(24)—N(4)	125.6 (2)
C(1)—N(2)—N(3)	114.5 (2)	C(25)—C(24)—N(4)	115.7 (2)
C(13)—N(3)—N(2)	114.2 (2)	C(25)—C(24)—C(23)	118.7 (2)
C(2)—C(1)—N(2)	123.4 (2)	C(24)—N(4)—N(5)	114.4 (2)
C(10)—C(1)—N(2)	116.5 (2)	C(27)—N(5)—N(4)	113.5 (2)
C(10)—C(1)—C(2)	120.1 (2)	C(28)—C(27)—N(5)	123.8 (2)
C(14)—C(13)—N(3)	125.5 (2)	C(36)—C(27)—N(5)	115.8 (2)
C(18)—C(13)—N(3)	115.7 (2)	C(36)—C(27)—C(28)	120.4 (2)
C(18)—C(13)—C(14)	118.8 (2)	C(29)—C(30)—N(6)	123.6 (2)
C(17)—C(16)—C(15)	117.1 (2)	C(31)—C(30)—N(6)	117.2 (2)
C(19)—C(16)—C(15)	120.2 (2)	C(31)—C(30)—C(29)	119.2 (2)
C(19)—C(16)—C(17)	122.7 (2)	C(37)—N(6)—C(30)	115.6 (2)
C(20)—C(19)—C(16)	127.1 (2)	C(38)—N(6)—C(30)	113.2 (2)
C(21)—C(20)—C(19)	127.5 (2)	C(38)—N(6)—C(37)	111.8 (2)
C(22)—C(21)—C(20)	119.2 (2)		

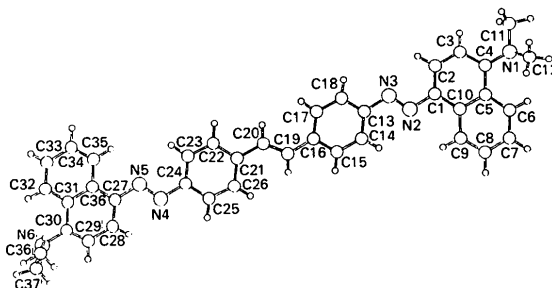


Fig. 1. Molecular structure of the title compound.

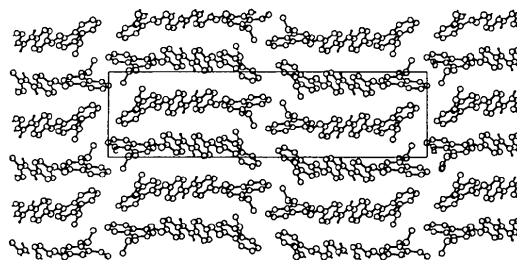


Fig. 2. Crystal structure of the title compound, viewed along [100].

sively) were localized step by step; all positional and anisotropic thermal parameters for C and N atoms were refined; the isotropic thermal parameters for H atoms were fixed using a factor of about 1.1 times the average value of the diagonal elements of the carrying atom. The final error indicators are $R = 0.053$ and $wR = 0.049$ with weights $w = 4.22/\sigma^2(F_o)$; $S = 2.27$; in the last refinement cycle $(\Delta/\sigma)_{\max} = 0.045$; $\Delta\rho_{\max}/\Delta\rho_{\min} = 0.21/-0.18 \text{ e \AA}^{-3}$; 499 parameters were refined. Atomic scattering factors from program *SHELX76* (Sheldrick, 1976), IBM 3090 computer.

Discussion. The final atomic parameters for N and C atoms are given in Table 1,* selected interatomic

* Lists of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53876 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances and angles in Table 2. The molecular structure is presented in Fig. 1, the molecular packing in Fig. 2.

All distances and angles lie within the range of values found for other compounds of a similar composition to the title compound. The angles between

the 'best' planes of the two halves of the molecule are listed in Table 3. As there is no centre of symmetry within the molecule, slightly different values are observed for the two corresponding groups.

The angle between the planes of the *trans*-stilbene moieties 3 and 3' (see Table 3) is 10.2°, in contrast to the value of 0° in the centrosymmetric molecule of the *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). The adjacent naphthyl and phenyl groups, linked by the diazo groups, form angles of 25.5 and 40.5°, respectively. These angles are greater than those found in other azo derivatives, e.g. *trans*-chloroazostilbene (Komeyama, Yamamoto, Nishimura & Hasegawa, 1973) or chloronitrophenylazonaphthol (Whitaker, 1977), 0 and 0.8°, respectively. This may be due to crystal packing forces.

The molecule can be described as quasi centrosymmetric and nearly planar, Fig. 1. The molecule is sufficiently planar to be conjugated with an absorbance maximum at 487 nm in chloroform solution, where it will occur in planar form. The distance from N(1) to N(6) which gives a measure for the length of the conjugated system is 24.65 (2) Å.

The *b* axis projection of the structure (Fig. 2) shows that the molecules are extended along [15,0,2]. The shortest intermolecular atomic distances are N(1)⋯C(33) = 3.567 (3) Å, and C(2)⋯C(19) =

Table 3. Angles (°) between the best planes of the subunits

Subunit	2	3	4	3'	2'	1'
1	18.0	25.5	20.9	15.3	0.6	25.2
2		7.5	3.0	2.7	17.5	43.2
3			4.6	10.2	25.0	50.7
4				5.6	20.4	46.1
3'					14.8	40.5
2'						25.7

Subunits: 1 = C(1)–C(10); 1' = C(27)–C(36); 2 = C(1), C(13), N(2), N(3); 2' = C(24), C(27), N(4), N(5); 3 = C(13)–C(18); 3' = C(21)–C(26); 4 = C(19), C(20), H(19), H(20).

3.507 (3) Å; the intermolecular bonding is entirely of a van der Waals type.

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References

- AFTERGUT, S. & COLE, H. S. (1979). General Electric Co., US Patent No. 2,834,7446.
 HOEKSTRA, A., MEERTENS, P. & VOS, A. (1975). *Acta Cryst.* B31, 2813–2817.
 KOMEYAMA, M., YAMAMOTO, S., NISHIMURA, N. & HASEGAWA, S. (1973). *Bull. Chem. Soc. Jpn*, 46, 2606–2607.
 SEKI, H., SHISHIDO, C., UCHIDA, T. & WADA, M. (1982). *Jpn J. Appl. Phys.* 21, 191–196.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 WHITAKER, A. (1977). *Z. Kristallogr.* 145, 271–288.

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Structure of 4-Aminopyridinium Dihydrogentetraoxophosphate(V) Monohydrate

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Abstract. C₅H₇N₂⁺·H₂PO₄⁻·H₂O, *M_r* = 210.1, triclinic, *P* $\bar{1}$, *a* = 8.951 (9), *b* = 7.982 (8), *c* = 7.398 (8) Å, α = 113.47 (5), β = 108.75 (5), γ = 77.18 (5)°, *V* = 456 (2) Å³, *Z* = 2, *D_x* = 1.529 g cm⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.7107 Å, μ = 2.866 cm⁻¹, *F*(000) = 220, *T* = 293 K, final *R* = 0.032 for 2292 independent observed reflections. This structure points to the formation of an (H₂PO₄·H₂O)_{*n*}⁻ layer polyanion on which the 4-aminopyridinium cations are anchored through hydrogen bonds originating from the amine donor groups. The role of water in the balance of ionic charges is emphasized.

Introduction. The crystal chemistry of alkyl and aryl cations encapsulated between chains or layers of

(H₂PO₄⁻)_{*n*} polyanions is fascinating because it may lead to the crystal engineering of polar materials. The various types of (H₂PO₄⁻)_{*n*} aggregates (= polyanions) observed in many crystal structures reveal the flexibility of the aggregation with respect to the chiral or achiral associated cations (Masse & Durif, 1990) and the possible interaction of the small dipole moments of the H₂PO₄ units with the dipole moments of the organic moieties, which may induce the acentricity of the future packing. The short hydrogen bonds between the H₂PO₄ units which build up the anionic layer structure cannot usually be disjoined by the reactivity of the organic functional groups. The ability of an hydroxyl radical to open the (H₂PO₄⁻)_{*n*} chains has been observed in *N,N*-