

is nearly the same as those values predicted for planar *cis*-amide bonds: 1.32–1.34 Å (Ramachandran & Sasisekharan, 1968; Winkler & Dunitz, 1975). If one compares the present results with a previous study on spirodilactams (Ealick & van der Helm, 1975, 1977; Ealick, Washecheck & van der Helm, 1976), it appears that the influence on the N–C' and C'–O distances becomes significant only when the non-planarity of the amide group is rather large, that is when $\chi_N \approx 2\tau \geq 10-15^\circ$.

The packing of the molecules is by H-bonding around the twofold screw axis [N(1)···O(2)(1 - x , $\frac{1}{2} + y$, $\frac{1}{2} - z$) 2.875 Å; H(1)···O(2) 2.071 Å and N(1)–H(1)···O(2) 155°], and by van der Waals forces in the *a* and *c* directions.

The research was supported by Grant GM-21822 from the National Institutes of Health. The authors wish to express their gratitude to Dr K. Bláha, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, for providing the sample used in this investigation. We also thank the University of Oklahoma for providing computer time.

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Acta Cryst. (1979). B35, 3103–3106

2,5-Distyrylpyrazine (DSP)—1,4-Bis[2-(2-pyridyl)vinyl]benzene (P2VB) (4 : 6); a Photopolymerizable Mixed Crystal

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(Received 6 August 1979; accepted 29 August 1979)

Abstract. C₂₀H₁₆N₂ (for each compound), $M_r = 284.4$, orthorhombic, *Pbca*, $a = 21.041$ (5), $b = 9.608$ (2), $c = 7.364$ (1) Å, $Z = 4$, $D_x = 1.267$ Mg m⁻³. The structure is isomorphous with the pure crystals; the molecules are arranged along *c*, displaced by about half a molecule, to form a photopolymerizable plane-to-plane stack. Only the internal rotations about single bonds differ from those of the pure crystals, and result in considerably shorter intermolecular contacts of reactive functional groups between DSP and DSP, and somewhat longer between P2VB and P2VB when compared with those in the pure crystals. The distance between DSP and P2VB molecules is intermediate, with the functional groups no longer parallel.

0567-7408/79/123103-04\$01.00

Introduction. DSP and P2VB, having the same formula and approximately similar molecular dimensions, crystallize from solution isomorphously in space group *Pbca*. (DSP is dimorphic and also crystallizes in the photostable modification of $P2_1/a$.) Both materials undergo four-centre-type photopolymerization in the crystalline state yielding a linear crystalline polymer with cyclobutane rings in the main polymer chain (Hasegawa, Suzuki, Nakanishi & Nakanishi, 1973). The quantum yield of the solid-state photopolymerization differs largely, however, between these two materials (about 30 times less for P2VB than for DSP) despite the fact that both molecules behave quite similarly in the solution oligomerization (Tamaki,

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Suzuki & Hasegawa, 1972; Suzuki, Tamaki & Hasegawa, 1974). Crystal structure analysis of P2VB and DSP has shown that there are no major differences in molecular packing (DSP: Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971; P2VB: Nakanishi, Ueno, Hasegawa & Sasada, 1972). This may suggest that certain marginal differences in geometry (e.g. the perpendicular distance between the planes of functional groups, a measure of the π - π interaction) may strongly affect the solid-state reactivity of these systems in particular and other photopolymerizable systems in general (Nakanishi, Jones, Thomas, Hasegawa & Rees, 1979). Consequently, the mixed crystal of DSP and P2VB is of interest, since we may expect only small changes in the crystal structure of the mixed crystal compared with those of pure crystals. The present study was therefore undertaken to reveal such structural changes and their relationship to subsequent photochemical behaviour.

Both compounds were prepared by previous methods (Hasegawa, Suzuki, Suzuki & Nakanishi, 1969), and purified by recrystallization from benzene. Finely ground crystals of DSP and P2VB (45:55), the formation of a solid solution for which had been confirmed by differential scanning calorimetry, were subjected to vacuum sublimation at a pressure of ~ 1 Pa at 473 K. Plate-like crystals were grown, together with a fine powdery deposit, on a water-cooled immersion condenser. The specimen used for structural analysis was a fragment of a plate, $0.1 \times 0.2 \times 0.2$ mm. The lattice constants and intensities were obtained from measurements on a Syntex P2₁ four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Reflections within the range of $2\theta < 150^\circ$ were collected in a 2θ - ω scan mode at a scanning rate of 4° min^{-1} . Of 1309 independent reflections collected, 1072 had $F_o > 5\sigma(F_o)$ and were used for the structure determination. No correction was made for absorption ($\mu = 0.116 \text{ mm}^{-1}$).

Since the mixed crystal is isomorphous with the pure crystals of DSP and P2VB and the cell dimensions are close to those of the pure crystals, an approximate structure was first selected with atomic coordinates of the pure crystals, giving $R = 0.30$. Starting from this, various least-squares refinements were carried out (i.e. different trial arrangements of atom-sharing and geometry constraints) to attain a reasonable solution. Full-matrix isotropic non-hydrogen-atom refinement gave $R = 0.125$ and site-occupancy factors of 0.37:0.63 (DSP:P2VB). The next stage of isotropic refinement (including geometrically positioned H atoms) reduced R to 0.095, giving rise to the occupancy factors of 0.40:0.60. Anisotropic refinement gave $R = 0.064$. No change in the occupancy factors occurred. Up to this stage the geometries of the benzene, pyridine and pyrazine rings were fixed at those present in the pure crystals. In the final refine-

ment, all the parameters were refined independently but with a block full-matrix for each molecule. The final R was 0.06.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates are given in Table 1 and the atom numbering is shown in Fig. 1.

All calculations were performed on an IBM 370-65 computer with *SHELX 76* (G. M. Sheldrick) and *PLUTO 78* (W. D. S. Motherwell).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34725 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) with e.s.d.'s in parentheses

	x	y	z
For P2VB			
C(1)	412 (1)	-1124 (3)	9820 (4)
C(2)	406 (2)	-123 (3)	8428 (5)
C(7)	-1 (2)	1031 (3)	8667 (4)
C(3)	840 (1)	-332 (4)	6924 (5)
C(4)	857 (2)	376 (4)	5339 (5)
C(5)	1279 (1)	38 (3)	3828 (4)
C(6)	1413 (2)	1076 (4)	2533 (5)
N(1)	1559 (1)	-1220 (3)	3741 (4)
C(8)	1817 (2)	763 (4)	1100 (5)
C(9)	1980 (2)	-1466 (4)	2430 (5)
C(10)	2079 (2)	-564 (3)	991 (5)
H(C1)	745 (6)	-1977 (7)	9728 (7)
H(C7)	-5 (7)	1845 (7)	7664 (7)
H(C3)	1177 (7)	-1140 (7)	7088 (7)
H(C4)	533 (6)	1242 (7)	5185 (7)
H(C6)	1208 (6)	2095 (7)	2663 (7)
H(C8)	1930 (6)	1534 (7)	81 (7)
H(C9)	2250 (6)	-2415 (7)	2496 (7)
H(C10)	2331 (6)	-883 (7)	-183 (7)
For DSP			
C(1)	278 (2)	-1224 (4)	9932 (6)
C(2)	364 (2)	-257 (4)	8545 (5)
N(1)	58 (2)	1012 (5)	8613 (6)
C(3)	741 (2)	-488 (4)	6918 (6)
C(4)	855 (2)	461 (5)	5627 (6)
C(5)	1264 (2)	282 (4)	4048 (6)
C(6)	1279 (2)	1213 (5)	2576 (6)
C(7)	1614 (2)	-953 (4)	3886 (5)
C(8)	1676 (2)	1034 (5)	1101 (6)
C(9)	1956 (3)	-1178 (4)	2293 (6)
C(10)	2064 (2)	-119 (4)	1045 (6)
H(C1)	502 (7)	-2223 (7)	9796 (7)
H(C3)	945 (7)	-1517 (7)	6728 (7)
H(C4)	625 (7)	1455 (7)	5776 (7)
H(C6)	947 (7)	2077 (7)	2586 (7)
H(C7)	1620 (7)	-1715 (7)	4966 (7)
H(C8)	1681 (7)	1790 (7)	14 (7)
H(C9)	2135 (7)	-2206 (7)	2023 (7)
H(C10)	2423 (7)	-203 (7)	65 (7)

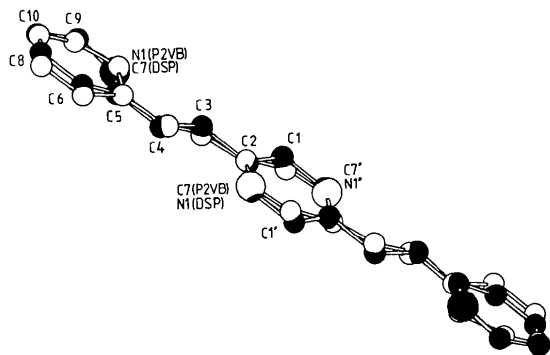


Fig. 1. The atomic numbering and the electron-sharing arrangements of the DSP and P2VB molecules.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

For P2VB

C(1)—C(2)	1.405 (5)	C(5)—C(6)	1.409 (5)
C(1)—C(7')	1.414 (5)	C(5)—N(1)	1.346 (4)
C(2)—C(7)	1.413 (4)	C(6)—C(8)	1.388 (5)
C(2)—C(3)	1.449 (5)	N(1)—C(9)	1.332 (5)
C(3)—C(4)	1.352 (5)	C(8)—C(10)	1.392 (5)
C(4)—C(5)	1.460 (5)	C(9)—C(10)	1.384 (5)

C(1)—C(2)—C(3)	117.2 (3)	C(4)—C(5)—N(1)	121.0 (3)
C(1)—C(2)—C(7)	116.8 (3)	C(5)—C(6)—C(8)	118.9 (3)
C(3)—C(2)—C(7)	125.9 (3)	C(5)—N(1)—C(9)	119.0 (3)
C(1')—C(7)—C(2)	121.4 (3)	C(6)—C(5)—N(1)	121.1 (3)
C(7')—C(1)—C(2)	121.8 (3)	C(6)—C(8)—C(10)	119.0 (3)
C(2)—C(3)—C(4)	127.4 (3)	N(1)—C(9)—C(10)	122.9 (3)
C(3)—C(4)—C(5)	124.2 (3)	C(8)—C(10)—C(9)	118.0 (3)
C(4)—C(5)—C(6)	118.7 (3)		

For DSP

C(1)—C(2)	1.392 (6)	C(5)—C(6)	1.405 (6)
C(1)—N(1')	1.300 (6)	C(5)—C(7)	1.402 (6)
C(2)—N(1)	1.380 (6)	C(6)—C(8)	1.382 (6)
C(2)—C(3)	1.455 (6)	C(7)—C(9)	1.394 (6)
C(3)—C(4)	1.338 (6)	C(8)—C(10)	1.376 (6)
C(4)—C(5)	1.457 (6)	C(9)—C(10)	1.390 (6)

C(1)—C(2)—C(3)	125.0 (4)	C(4)—C(5)—C(7)	118.5 (4)
C(1)—C(2)—N(1)	120.2 (4)	C(5)—C(6)—C(8)	122.7 (4)
N(1)—C(2)—C(3)	114.8 (4)	C(5)—C(7)—C(9)	118.3 (4)
C(1')—N(1)—C(2)	114.9 (4)	C(6)—C(5)—C(7)	117.5 (4)
N(1')—C(1)—C(2)	125.2 (4)	C(6)—C(8)—C(10)	118.8 (4)
C(2)—C(3)—C(4)	125.3 (4)	C(7)—C(9)—C(10)	121.8 (4)
C(3)—C(4)—C(5)	126.3 (4)	C(8)—C(10)—C(9)	118.2 (4)
C(4)—C(5)—C(6)	123.6 (4)		

Discussion. Bond lengths and angles are listed in Table 2 and are similar to those in the pure crystals. The central aromatic rings and ethylenic groups of both molecules are planar within 0.029 Å. Terminal aromatic rings, *i.e.* pyridine for P2VB and benzene for DSP, are not planar due to deformation at C(9) and C(10); moieties consisting of the remaining four atoms are planar. In P2VB, referring to the central benzene ring, the ethylenic plane rotates 9.4 (3)° (1.9° in pure

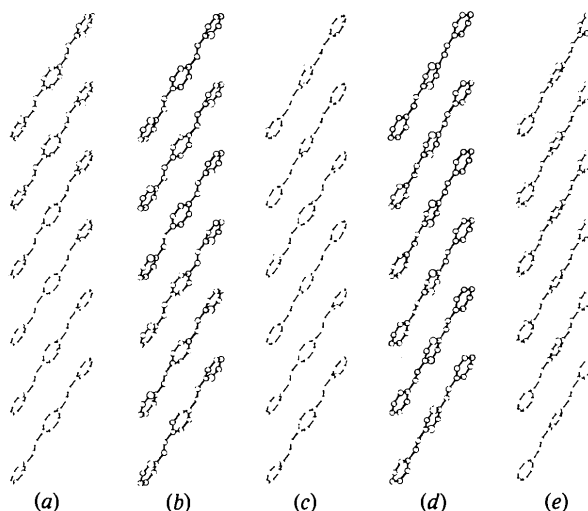


Fig. 2. The stacking arrangement, viewed along *b*, of P2VB molecules in (a) the pure crystal and (b) the mixed crystal. The arrangement of DSP and P2VB in the mixed crystal is shown in (c), whilst (d) and (e) give the arrangements of DSP in the mixed and pure crystals respectively.

P2VB) about C(3)—C(4), and the pyridine 19.0 (3)° (11.8°) about C(4)—C(5) in the opposite direction. Thus, the dihedral angle between the benzene and pyridine rings is 9.8 (3)° (10.6°). In DSP, the corresponding values are 4.3 (4)° (9.4°), 7.8 (4)° (2.6°) and 4.2 (4)° (12.1°) respectively. Despite the similarity of cell dimensions between the mixed crystal and pure P2VB [$a = 21.060$ (9), $b = 9.567$ (5), $c = 7.311$ (4) Å], the P2VB molecule has a significantly different conformation from that found in the pure crystal. The DSP molecule becomes more planar than in the pure crystal [$a = 20.638$ (10), $b = 9.599$ (5), $c = 7.655$ (4) Å].

The molecular-packing modes are, in principle, identical to those of the pure crystals; molecules are stacked along *c*, displaced by about half a molecule in the direction of the molecular long axis, to form a photopolymerizable plane-to-plane stack (Nakanishi, Ueno & Sasada, 1978). The arrangements of molecules in the stack viewed along *b* are shown in Fig. 2. Figs. 2(d) and (e) demonstrate that DSP molecules in the mixed crystal take up a conformation in which the pyrazine and benzene rings become more parallel than in the pure crystal.

The distance of 3.941 (6) Å between adjacent P2VB molecules is longer than that in the pure crystal (3.910 Å), whereas the distance between DSP molecules, 3.846 (7) Å, is shorter than that in the pure crystal (3.939 Å) and is the shortest intermolecular distance known among the diolefin crystals (Nakanishi *et al.*, 1979). The perpendicular distance between ethylenic planes of P2VB molecules,

3.56 Å, is very close to the value of 3.55 Å for DSP molecules. The former is identical to that of pure P2VB but the latter is rather longer than that of pure DSP (3.49 Å). Between P2VB and DSP the corresponding interatomic distance is 3.752 (6) Å from C(4) of P2VB to C(3) of DSP, and 4.033 (6) Å from C(3) of P2VB to C(4) of DSP. Thus, the double bonds are no longer parallel.

The relationship between these geometric factors and photochemical and spectroscopic behaviour will be described elsewhere.

We acknowledge the support of the Science Research Council and the Oppenheimer Fund of the University of Cambridge. We are grateful to Dr P. Raithby for his assistance and appreciate the stimulus provided by Professors J. M. Thomas and M. Hasegawa.

Acta Cryst. (1979). B35, 3106–3109

Structure of 1-[(3,4-Dichlorophenyl)methoxy]-1,6-dihydro-6,6-dimethyl-1,3,5-triazine-2,4-diamine Hydrochloride 0.29-Hydrate

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(Received 24 January 1978; accepted 4 September 1979)

Abstract. $C_{12}H_{16}Cl_2N_5O^+ \cdot Cl^- \cdot 0.29H_2O$, $M_r = 357.7$, monoclinic, $P2_1/c$, $a = 5.989$ (1), $b = 8.000$ (1), $c = 34.143$ (3) Å, $\beta = 91.32$ (2)°, D_{obs} (aqueous KI) = 1.452, $D_{calc} = 1.453$ Mg m⁻³ for $Z = 4$; Mo $K\alpha$ diffractometer data; final $R = 0.046$. The dihydrotriazine nucleus is protonated at N(5), a position which maximizes positive-charge delocalization. All of the H atoms on N are involved in either H...N or H...Cl contacts, with the exception of one H on N(4). This H atom forms a 1.9 Å contact with a *ca* 2 e Å⁻³ atom, which we have arbitrarily treated as an O atom, believing it to be due to a disordered water molecule.

Introduction. The most widespread of all human parasitic diseases is malaria, afflicting substantial numbers of people over a large geographical area. The disease is one of the most common causes of death today. Malaria is transmitted by the Anopheles mosquito, and control and eradication of the disease

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have been achieved in many regions through extensive insecticide spraying programs, destruction of breeding areas, etc. Chemotherapy has been very successful in the control and treatment of the disease, although in recent years drug-refractory strains of malaria have emerged.

The mechanisms of action of the majority of anti-malarial drugs fall into two general categories: (1) antifolates; (2) interactions with DNA. The title compound was first reported to have antimalarial activity in 1969, and it was found to be active against both sensitive and several drug-resistant strains of *Plasmodium berghei* in mice. Its mechanism of action is that of an antifolate (Lee, Heiffer & Kinter, 1976; Genter & Smith, 1977). We have been interested in antimalarial structures for some time, and the present study gave us the opportunity of obtaining accurate structural data for a cyclic biguanidinium compound for comparison with an acyclic form (III; Ammon & Plastas, 1973). We were particularly interested in the position of protonation of the dihydrotriazine nucleus. Although earlier work (Bailey, 1954) on the HCl and

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