Photostable Modification of 2,5-Distyrylpyrazine (DSP)

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Abstract. $C_{20}H_{16}N_2$, M.W. 284·4, monoclinic, $P2_1/a$, $a = 13·833$ (6), $b = 18·615$ (10), $c = 5·823$ (5) Å, $\beta = 92·63$ (5)°. $Z = 4$, $D_x = 1·261$, $D_m = 1·269$ g cm^{-3}. The non-planar molecules, in which two benzene rings make a dihedral angle of 52·3°, are arranged so that the molecular long axis is nearly perpendicular to the a axis, forming a layered structure with intervals of about $a/4$. The shortest intermolecular distance between functional double bonds is 4·187 Å.

Introduction. DSP crystallizes in two modifications: the α-form from solution and the γ-form by sublimation (Nakanishi, Hasegawa & Sasada, 1972). The crystal structure of the photopolymerizable α-form (Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971) has been discussed in relation to the mechanism of the solid-state polymerization which results in the formation of a three-dimensionally oriented polymer containing a cyclobutane ring in the main chain (Nakanishi, Hasegawa & Sasada, 1972). The crystal structure analysis of the photostable γ-form was undertaken as a part of studies which aim to clarify the relation between photoreactivity and molecular arrangement.

Fine crystals of the α-form of DSP were prepared according to the previous paper (Hasegawa, Suzuki, Suzuki & Nakanishi, 1969) and were subjected to vacuum sublimation at 200 °C. Needle-shaped crystals of the γ-form were grown together with powder-like

Table 1. *Fractional coordinates* ($\times 10^4$ *for* N, C; $\times 10^3$ *for* H) *and thermal parameters* ($\times 10^3$)

The anisotropic thermal parameters are described by $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$. Estimated standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1172 (3)	142 (2)	4333 (7)	6·8 (3)	2·2 (2)	27 (2)	0·1 (4)	4 (1)	−0·4 (8)
C(1)	1127 (4)	94 (3)	267 (9)	7·0 (4)	2·3 (2)	24 (2)	0·2 (4)	1 (1)	−2·1 (10)
C(2)	1218 (4)	482 (3)	2332 (8)	4·9 (3)	2·0 (2)	20 (2)	−0·6 (4)	4 (1)	1·2 (9)
C(3)	1293 (4)	1268 (3)	2338 (9)	5·9 (4)	2·3 (2)	24 (2)	0·5 (4)	3 (1)	2·6 (10)
C(4)	1195 (4)	1666 (3)	4209 (9)	5·7 (4)	2·3 (2)	25 (2)	0·1 (4)	2 (1)	1·9 (9)
C(5)	1303 (4)	2442 (3)	4410 (8)	4·8 (3)	2·1 (2)	21 (2)	0·5 (4)	1 (1)	−0·3 (9)
C(6)	992 (4)	2779 (3)	6376 (9)	6·7 (4)	2·1 (2)	26 (2)	−0·3 (4)	6 (1)	0·2 (10)
C(7)	1734 (4)	2870 (3)	2745 (9)	5·8 (4)	3·0 (2)	25 (2)	−0·4 (4)	2 (1)	2·7 (10)
C(8)	1069 (4)	3528 (3)	6649 (10)	6·9 (4)	2·9 (2)	20 (3)	−0·9 (5)	3 (1)	−3·3 (11)
C(9)	1816 (4)	3602 (3)	3045 (10)	7·0 (4)	2·3 (2)	31 (2)	−0·9 (5)	6 (1)	3·9 (10)
C(10)	1470 (5)	3933 (3)	4958 (10)	7·7 (4)	2·3 (2)	32 (2)	−0·5 (5)	−1 (2)	−2·3 (11)
N(1′)	1211 (4)	−618 (2)	182 (7)	7·5 (3)	2·2 (1)	20 (1)	−0·3 (4)	4 (1)	−0·2 (8)
C(1′)	1138 (4)	−575 (3)	4250 (8)	7·0 (4)	2·4 (2)	16 (2)	0·1 (4)	1 (1)	−0·3 (9)
C(2′)	1169 (4)	−963 (3)	2215 (9)	4·3 (3)	2·6 (2)	21 (2)	0·3 (4)	−1 (1)	0·4 (9)
C(3′)	1210 (4)	−1746 (3)	2235 (9)	6·3 (4)	2·2 (2)	26 (2)	−0·1 (4)	1 (1)	1·1 (10)
C(4′)	1122 (4)	−2168 (3)	393 (9)	4·9 (3)	2·3 (2)	22 (2)	0·1 (4)	−0 (1)	0·6 (9)
C(5′)	1189 (4)	−2953 (3)	376 (9)	4·6 (3)	2·2 (2)	27 (2)	0·3 (4)	1 (1)	−0·8 (10)
C(6′)	839 (4)	−3335 (3)	−1539 (9)	6·6 (4)	3·0 (2)	24 (2)	0·9 (5)	−3 (1)	−0·4 (10)
C(7′)	1600 (4)	−3334 (3)	2220 (9)	5·9 (3)	2·5 (2)	26 (2)	−0·0 (4)	−2 (1)	1·2 (10)
C(8′)	875 (5)	−4073 (4)	−1580 (12)	8·2 (5)	3·1 (2)	42 (3)	0·4 (5)	1 (2)	−7·1 (13)
C(9′)	1649 (5)	−4079 (3)	2156 (11)	7·6 (4)	2·8 (2)	37 (2)	1·4 (5)	−2 (2)	4·2 (12)
C(10′)	1272 (5)	−4450 (3)	273 (12)	7·6 (4)	3·1 (2)	48 (3)	0·4 (5)	−4 (2)	−3·9 (12)

	x	y	z	B (Å²)	C–H (Å)		x	y	z	B (Å²)	C–H (Å)
H(C1)	123 (4)	36 (3)	−120 (10)	4 (1)	0·99 (6)	H(C1′)	112 (4)	−85 (3)	582 (9)	3 (1)	1·05 (6)
H(C3)	144 (4)	152 (3)	84 (9)	3 (1)	1·02 (6)	H(C3′)	135 (4)	−200 (3)	387 (9)	2 (1)	1·07 (6)
H(C4)	104 (3)	139 (3)	557 (9)	2 (1)	0·98 (5)	H(C4′)	99 (3)	−192 (3)	−110 (9)	2 (1)	1·00 (5)
H(C6)	71 (4)	253 (3)	765 (9)	3 (1)	0·98 (5)	H(C6′)	53 (4)	−305 (3)	−284 (10)	4 (2)	1·00 (6)
H(C7)	188 (4)	265 (3)	132 (9)	2 (1)	0·95 (5)	H(C7′)	192 (4)	−306 (3)	349 (9)	3 (1)	0·99 (6)
H(C8)	85 (5)	378 (4)	814 (11)	5 (2)	1·05 (7)	H(C8′)	66 (5)	−432 (4)	−295 (13)	8 (2)	0·96 (8)
H(C9)	213 (5)	389 (4)	188 (11)	5 (2)	0·98 (7)	H(C9′)	199 (4)	−433 (3)	357 (10)	3 (1)	1·04 (6)
H(C10)	157 (5)	446 (4)	523 (12)	7 (2)	1·00 (7)	H(C10′)	127 (4)	−497 (3)	24 (10)	4 (2)	0·97 (6)

crystals of the α-form. The specimen used was a fragment of a needle, 0·10 × 0·10 × 0·15 mm. The space group was determined from photographs. The precise

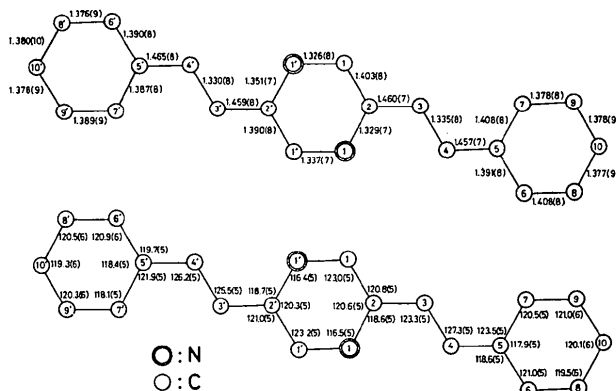Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.
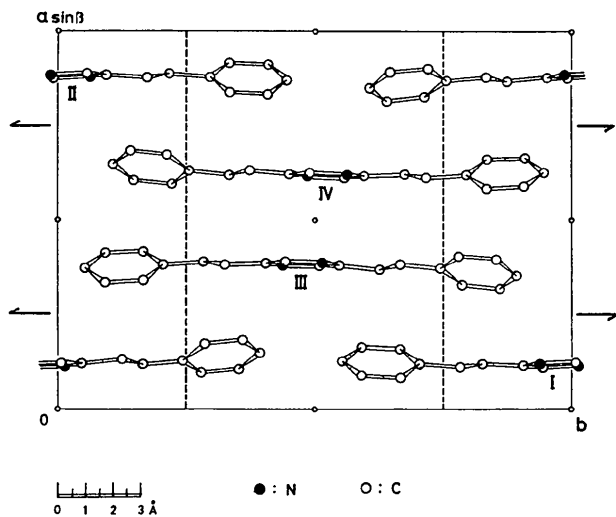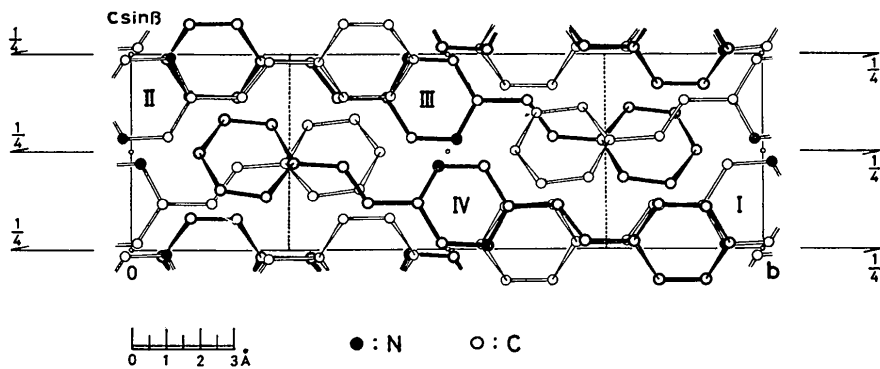

Fig. 2. The crystal structure viewed along c.

lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. All reflexions within the range of $2\theta < 50°$ were collected by use of the $2\theta-\omega$ scan mode with a scanning rate of 2° min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. Of 2564 reflexions, 1354 were greater in intensity than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption ($\mu = 0·87$ cm^{-1}).

By iterative symbolic addition procedures, the signs of 250 reflexions out of 321 with $|E| \geq 1·5$ were determined in terms of a symbol. The corresponding E maps showed two images of the molecule along b, which are related by a translation vector equal to one of the repeating interatomic vectors in the structure. The correct position of the molecule was found to be halfway between the two images, just as suggested by Ahmed (1974). The parameters were refined by the block-diagonal least-squares method using $\omega = 0·5$ for $|F_o| \leq 1·0$, $1·0$ for $|F_o| > 1·0$. Isotropic H atoms were first located geometrically and then refined. The final R was 0·073.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates and thermal parameters are given in Table 1.

Discussion. The molecular structure and the numbering system used are shown in Fig. 1. The bond lengths and angles are similar to those in the α-form, except for the fairly short C(2)–N(1) bond and the somewhat small angle C(2)–C(3)–C(4). The pyrazine ring, benzene rings A [C(5)–C(10)] and B [C(5′)–C(10′)], and ethylene groups A [C(2)–C(5)] and B [C(2′)–C(5′)] are planar within a deviation of 0·015 Å from the respective

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* A list of structure factors and a table of deviations of atoms from some least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31938 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 3. The crystal structure viewed along a.

mean planes.* The molecule as a whole is not in a planar conformation, contrary to the nearly planar structure in the α-form. From the plane of the pyrazine ring, the ethylene A rotates by 8·6° about the bond C(2)–C(3), and the benzene A by 13·0° about C(4)–C(5) in the same direction. Furthermore, in the opposite direction, the ethylene B rotates by 10·9° about C(2')–C(3') and the benzene B by 17·2° about C(4')–C(5'). Thus, the pyrazine ring makes dihedral angles of 23·5 and 28·9° with benzenes A and B respectively. The dihedral angle between the two benzene planes is 52·3°. It should be noted that the internal rotation about the bonds C(2)–C(3) and C(2')–C(3') (8·2 and 10·9°) is very close to that in the α-form (9·4°) with an entirely different type of packing. This is probably because of the nonbonded interaction between the lone-pair electron of the N atom and π electron of the ethylenic moiety.

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* See previous footnote.

Table 2. *Intermolecular distances between double bonds*

If this crystal was photoreactive, to form a cyclobutane ring the atomic pair indicated with an asterisk could be changed into a bond. Otherwise, extremely large molecular movement such as rotation would be required. General coordinates of the molecules are (x,y,z) for molecule 1, $(-x, -y, -z)$ for 2, $(0·5-x, 0·5+y, -z)$ for 3, $(0·5-x, 0·5+y, 1·0-z)$ for 4 and $(-x, -y, 1·0-z)$ for 5.

Atom in molecule 1	Atom in molecule		Distance (Å)
C(3)	C(3')	2	4·369*
C(3)	C(4')	2	4·009
C(4)	C(3')	2	4·901
C(4)	C(4')	2	4·187*
C(3)	C(3')	3	5·791*
C(3)	C(4')	3	4·931
C(4)	C(3')	3	6·079
C(4)	C(4')	3	5·158*
C(3)	C(3')	4	5·882*
C(3)	C(4')	4	6·148
C(4)	C(3')	4	5·024
C(4)	C(4')	4	5·226*
C(3)	C(3')	5	4·882*
C(3)	C(4')	5	5·766
C(4)	C(3')	5	4·000
C(4)	C(4')	5	4·684*

The crystal structure viewed along **c** and **a** is shown in Figs. 2 and 3 respectively. A parallel plane-to-plane stack, which is a common feature of packing of photopolymerizable crystals (Sasada *et al.*, 1971; Nakanishi, Ueno, Hasegawa & Sasada, 1972; Nakanishi, Ueno & Sasada, 1976), is not found in the present crystal. The molecules are arranged nearly perpendicular to the a axis, forming a layered structure with intervals of about $a/4$. The shortest distances between functional double bonds, 4·187 and 4·369 Å, are found for a pair of molecules which are in adjacent layers and related by a centre of symmetry (Table 2). Though the double bonds with short contacts in the γ-form are not parallel to each other, the shortest distance (4·187 Å) is not very much longer than those in the photopolymerizable crystals (3·92 Å on the average). In fact, it is within the range of photodimerizable separation (Bregman, Osaki, Schmidt & Sonntag, 1964). Therefore, the photostability of the γ-form should be ascribed to the present characteristic layered structure which suppresses the molecular deformation necessary for the cycloaddition reaction.

References

AHMED, F. R. (1974). *Acta Cryst.* B30, 2558–2564.
BREGMAN, J., OSAKI, K., SCHMIDT, G. M. J. & SONNTAG, F. I. (1964). *J. Chem. Soc.* pp. 2021–2030.
HASEGAWA, M., SUZUKI, Y., SUZUKI, F. & NAKANISHI, H. (1969). *J. Polym. Sci.* A1, (7), 743–752.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
NAKANISHI, H., HASEGAWA, M. & SASADA, Y. (1972). *J. Polym. Sci.* A2, (10), 1537–1553.
NAKANISHI, H., UENO, K., HASEGAWA, M. & SASADA, Y. (1972). *Chem. Lett.* pp. 301–304.
NAKANISHI, H., UENO, K. & SASADA, Y. (1976). *Acta Cryst.* B32, 1616–1618.
SASADA, Y., SHIMANOUCHI, H., NAKANISHI, H. & HASEGAWA, M. (1971). *Bull. Chem. Soc. Japan*, 44, 1262–1270.