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The Crystal and Molecular Structure of 2,5-Distyrylpyrazine

Yoshio Sasada, Hirotaka Shimanouchi, Hachiro Nakanishi,* and Masaki Hasegawa*
Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Meguro-ku, Tokyo
**Research Institute for Polymers and Textiles, Kanagawa-ku, Yokohama*

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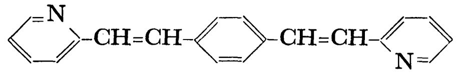
2,5-Distyrylpyrazine($C_{20}H_{16}N_2$), which has photo-polymerizability in the crystalline state, crystallizes in the orthorhombic system with cell dimensions of $a=20.638$, $b=9.599$, and $c=7.655$ Å, including four molecules in the unit cell. The space group is *Pbca*. The structure has been determined by the direct method and refined by the block-diagonal-matrix least-squares method using three-dimensional data. The molecules is not planar; the average plane of the pyrazine ring makes a dihedral angle of 12.09° with that of the benzene ring. The molecules are spaced by the *c*-translation forming an almost parallel plane-to-plane stack. In this stack, the ethylenic double bonds approach each other at the shortest intermolecular distances of 3.939 Å, since the long axis of the molecule makes an angle of about 30° with the *c*-axis. Therefore, the polymerization may occur between these double bonds to form a cyclobutane ring.

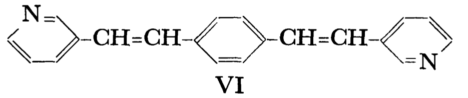
Recently, Hasegawa and his collaborators have reported that 2,5-distyrylpyrazine (DSP) (I) is polymerized by photo-irradiation in the crystalline state to result in a linear polymer (II) containing a cyclobutane ring in the main chain.[1,2]

In the course of exploring the photo-polymerizability of various related diolefinic compounds, it has been found that 1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB) (III) gives a polymer just like DSP.[2] Under a polarizing microscope, both polymers look like aggregates of bar-like crystals which are elongated in the direction of the *c*-axis of the monomer crystal.[3] The crystallinity of these polymers corresponds to the highest among known polymers.

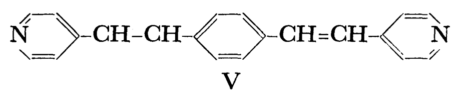
In order to investigate the mechanism of polymerization, X-ray powder photographs have been taken for these two monomers and the related diolefinic compounds.[4] The powder diagrams of DSP and P2VB are nearly identical with each other.



III



VI



V

On the other hand, 1,4-bis[β-pyridyl-(3)-vinyl]benzene (P3VB) (IV) and 1,4-bis[β-pyridyl-(4)-vinyl]benzene (P4VB) (V), which have nearly the same molecular dimensions as P2VB, give X-ray patterns different from those of I and III, and do not polymerize under the same conditions. These observations suggest that the molecules of DSP and P2VB are favourably arranged for polymerization in the crystal, while P3VB and P4VB are not.

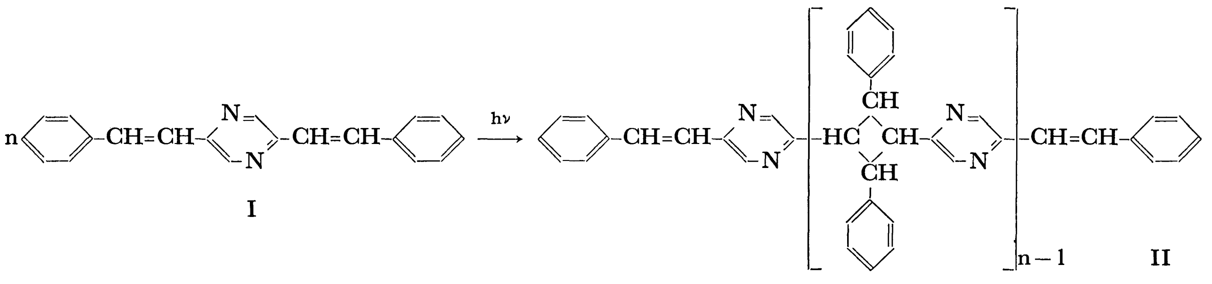
Moreover, the results of the analysis of kinetic behavior indicate that the polymerization of DSP is controlled by the molecular arrangement in the monomer crystal.[3]

The present paper will deal with the crystal structure of DSP as one of a series of studies aiming to clarify the relationship between the polymerization mechanism and the molecular arrangement in the crystal.

Experimental

DSP was prepared by the dehydration of 1 mol of 2,5-dimethylpyrazine and 2 mol of benzaldehyde in the presence of benzoic anhydride. By the slow evaporation of a saturated THF solution at room temperature, crystals suitable for the X-ray work were obtained. They were yellowish-green hexagonal plates with a thickness of about 1 mm.

The unit cell dimensions were determined by the least-squares treatment of the spacing of high-angle *hk*0 and *h*0*l* reflections, which were measured on Weissenberg photographs and calibrated with the powder lines of Al-wire. The density calculated by assuming 4 molecules in a unit cell, is 1.244 g·cm^{-3}, while the density measured by floatation is 1.257



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[1] M. Hasegawa and Y. Suzuki, *J. Polymer Sci., Part B* 5, 813 (1967).

[2] M. Hasegawa, Y. Suzuki, F. Suzuki, and H. Nakanishi, *ibid., Part A-1,* **7**, 743 (1969).

[3] H. Nakanishi, Y. Suzuki, F. Suzuki, and M. Hasegawa, *ibid., Part A-1,* **7**, 753 (1969).

[4] M. Iguchi, H. Nakanishi, and M. Hasegawa, *ibid., Part A-1,* **6**, 1055 (1968).

$g\cdot cm^{-3}$. From the systematic absences of reflections, the space group is determined to be *Pbca*; the absent reflections are 0*kl* when *k* is odd, *h*0*l* when *l* is odd, and *hk*0 when *h* is odd. Since the general positions are eight-fold in this space group, the number of the molecules in the unit cell indicates that the molecule must have a centre of symmetry. The crystal data of DSP are given in Table 1.

TABLE 1. CRYSTALLOGRAPHIC AND PHYSICAL DATA

Formula	$C_{20}H_{16}N_2$
MW	284
Mp	230°C
Crystal system	Orthorhombic
Space group	*Pbca*
a	20.638 Å
b	9.599 Å
c	7.655 Å
Z	4
Vol.	1517 Å^3
D_{calcd}	1.244 $g\cdot cm^{-3}$
D_{obsd}	1.257 $g\cdot cm^{-3}$
μ	6.83 cm^{-1}
F(000)	600

The intensity data were collected from equi-inclination multiple-film Weissenberg photographs. The layers from 0 to 5 along the *c*-axis and from 0 to 7 along the *b*-axis were recorded using Cu-Kα radiation. The crystals used had cross sections, perpendicular to the rotation axis, of 0.10×0.05 cm and of 0.05×0.05 cm for the *c*- and *b*-axis rotations respectively. The intensities were measured visually by comparison with a calibrated scale prepared with the same crystal. Of these 1246 reflections, 297 were measured as having zero intensity, while the others range from 1 to 19837 in their relative intensities. Corrections were made for the Lorentz and polarization factors and for spot size, but not for absorption. The data were put onto an absolute scale by means of Wilson's plot. The structure factors, $|F_h|$, and the normalized structure factors, $|E_h|$, were computed together.

Structure Determination

The symbolic addition procedure was applied for sign determination. As a starting set, the signs of five strong reflections were chosen; three of them specified the origin, and the other two were symbols, as is shown in Table 2. After six cycles of the phase-determining process using the $\sum_2$ relationship, the signs of 103 reflections out of 180 with $|E_h|>1.5$ were determined in terms of the *a* and *b* with a probability greater than 0.97. Further, by investigating the list of the $\sum_2$ relations, it seemed most probable that $a=+$ and $b=-$.

An E-map was computed using these 103 reflections with $a=+$ and $b=-$. All eleven non-hydrogen atoms in the asymmetric unit were well resolved in the resulting E-map, as is shown in Fig. 1. Two additional appreciable peaks appeared, one of which is at the centre of the pyrazine ring, and the other, at the centre of the benzene ring; they were easily excluded as being insignificant. The only ambiguity was in the choice of the position of the N atom from between the alternative assignments.

TABLE 2. ASSIGNMENT OF SIGNS OF FIVE STRONG REFLECTIONS

h	*k*	*l*	*E*	Sign
1	1	7	4.31	+
3	7	6	3.95	+
4	1	1	3.24	+
12	4	4	5.04	*a*
3	7	2	3.12	*b*

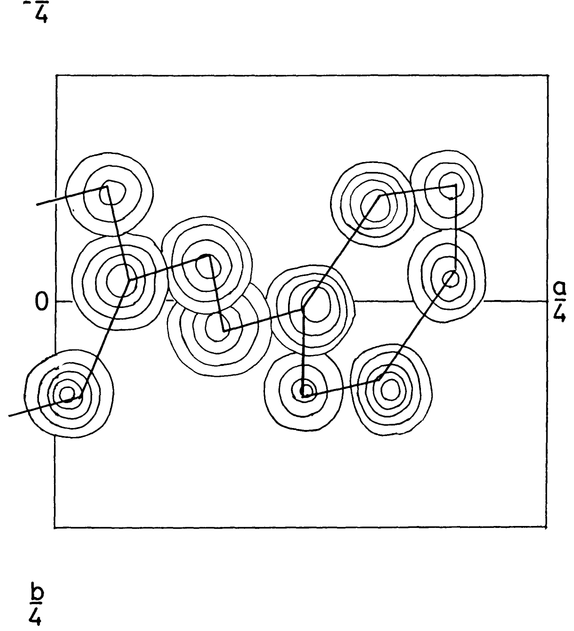

Fig. 1. Composite E-map. Contours are at equal intervals on an arbitrary scale. The final molecular shape is indicated with solid line.

Refinement

The coordinates of the eleven atoms as read on the E-map were subjected to Fourier refinement. On the first electron-density distribution map, the N atom was assigned easily from the peak height. The discrepancy factor, $R=\sum|F_o|-|F_c|/\sum|F_o|$, was 0.284 for the observed reflections. The parameters were refined by the block-diagonal-matrix least-squares method using isotropic temperature factors for all the atoms. After four cycles, the *R* value was reduced to 0.150. Further refinement was performed by introducing anisotropic temperature factors of the $exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$ form. After four cycles, the *R* value became 0.132. A difference Fourier synthesis at this stage revealed all the hydrogen atoms. The absence of a residual peak outside the N atom proved that the assignment of nitrogen based on the peak height was correct. The subsequent refinement was, however, initiated by using the positions of hydrogens computed by assuming suitable geometries of the C–H bond (C–H=1.08 Å), and the parameters of all the atoms including isotropic hydrogens were refined. After four cycles, the *R* value was 0.098. In the final cycles of refinement, the strongest reflection, 020, was excluded because it seemed to suffer from extinction. After four cycles, the *R* value reached 0.086.

The final atomic coordinates and the temperature factors are given in Table 3, and their standard deviations, in Table 4. The observed and calculated structure factors are listed in Table 5. The final three-dimensional electron density distribution is shown in Fig. 2.

The atomic scattering factors used in the calculation were taken from the International Tables for X-ray Crystallography (1962). The computations were done on CDC 3600 and HITAC 5020E computers with the programs written by T. Ashida.

Results and Discussion

Molecular Structure. The bond lengths and angles are listed in Table 6, along with their standard deviations; they are also shown in Fig. 3.

The mean value of the C–C bond lengths in the benzene ring is 1.397 Å, very close to that given by Sutton.[5] The C(6)–C(5)–C(7) angle, 117.7°, is somewhat smaller than the others. A decrease in the corresponding angle is observed in the benzene ring with the –CH=CHR substituent: 118.2 and 117.5° in 1,1-di-*p*-toluylethylene,[6]

TABLE 3. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS
The anisotropic temperature factors are expressed in the form of $exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

Atom	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{13}	B_{13}	B_{23}
N(1)	0.0111	0.1073	0.8780	0.00294	0.00982	0.01939	0.00071	0.00195	0.00074
C(1)	0.0254	−0.1253	0.9812	0.00291	0.00911	0.02153	0.00115	0.00139	0.00043
C(2)	0.0367	−0.0223	0.8568	0.00275	0.01040	0.01563	0.00004	0.00074	0.00093
C(3)	0.0771	−0.0504	0.7043	0.00304	0.00957	0.01857	0.00046	0.00124	−0.00197
C(4)	0.0848	0.0331	0.5676	0.00263	0.00980	0.01896	−0.00002	0.00051	−0.00129
C(5)	0.1252	0.0074	0.4135	0.00253	0.01030	0.01648	−0.00057	−0.00131	−0.00327
C(6)	0.1257	0.1050	0.2760	0.00331	0.01129	0.01886	−0.00075	−0.00060	0.00110
C(7)	0.1638	−0.1118	0.3953	0.00288	0.01178	0.01732	0.00042	0.00051	−0.00079
C(8)	0.1644	0.0848	0.1301	0.00409	0.01470	0.02104	−0.00276	0.00272	0.00287
C(9)	0.2024	−0.1323	0.2492	0.00314	0.01393	0.02249	0.00005	0.00139	−0.00750
C(10)	0.2029	−0.0338	0.1158	0.00372	0.01702	0.02048	−0.00233	0.00399	−0.00461
H(1)	0.0484	−0.2214	0.9619	6.10					
H(3)	0.1029	−0.1503	0.7026	6.14					
H(4)	0.0587	0.1307	0.5702	6.11					
H(6)	0.0950	0.1958	0.2855	5.66					
H(7)	0.1629	−0.1890	0.4978	5.72					
H(8)	0.1653	0.1624	0.0321	6.10					
H(9)	0.2337	−0.2227	0.2395	5.68					
H(10)	0.2339	−0.0463	0.0065	5.78					

TABLE 4. ESTIMATED STANDARD DEVIATIONS
($\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11}$ or $B)$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
N(1)	0.0039	0.0038	0.0040	0.00011	0.00045	0.00083	0.00038	0.00052	0.00113
C(1)	0.0048	0.0046	0.0052	0.00013	0.00052	0.00107	0.00046	0.00066	0.00134
C(2)	0.0045	0.0046	0.0046	0.00013	0.00054	0.00088	0.00045	0.00058	0.00124
C(3)	0.0049	0.0045	0.0049	0.00014	0.00052	0.00103	0.00046	0.00063	0.00133
C(4)	0.0046	0.0045	0.0049	0.00012	0.00053	0.00099	0.00044	0.00061	0.00130
C(5)	0.0044	0.0045	0.0047	0.00012	0.00054	0.00090	0.00044	0.00058	0.00126
C(6)	0.0051	0.0048	0.0052	0.00015	0.00059	0.00107	0.00052	0.00067	0.00142
C(7)	0.0048	0.0049	0.0049	0.00014	0.00059	0.00096	0.00048	0.00062	0.00139
C(8)	0.0058	0.0056	0.0056	0.00018	0.00074	0.00118	0.00063	0.00078	0.00163
C(9)	0.0052	0.0053	0.0058	0.00015	0.00066	0.00116	0.00055	0.00073	0.00164
C(10)	0.0056	0.0058	0.0056	0.00017	0.00081	0.00116	0.00064	0.00076	0.00176
H(1)	0.0508	0.0587	0.0586	1.61					
H(3)	0.0540	0.0567	0.0581	1.62					
H(4)	0.0544	0.0586	0.0577	1.60					
H(6)	0.0508	0.0526	0.0576	1.55					
H(7)	0.0512	0.0532	0.0573	1.55					
H(8)	0.0535	0.0563	0.0581	1.60					
H(9)	0.0501	0.0553	0.0569	1.50					
H(10)	0.0538	0.0550	0.0558	1.57					

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[5] L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958). S 13.

[6] G. Casalone, A. Gavezotti, C. Mariani, A. Mugnoli, and M. Simonetta, *Acta Crystallogr.*, **B26**, 1 (1970).

TABLE 5. OBSERVED AND CALCULATED STRUCTURE FACTORS
Both structure factors are multiplied by 4.5.

H	FO	FC
K,L= 0 0		
2	249	275
4	122	-131
6	272	287
8	36	-32
10	111	113
12	13	-9
14	33	29
16	33	-34
18	60	-57
20	63	-55
22	37	-37
24	57	62
K,L= 1 0		
2	52	57
4	105	-108
6	269	295
8	10	-13
10	17	-19
12	10	11
14*	0	0
16*	0	8
18	43	-43
20*	0	-2
22*	0	-8
24	27	-23
K,L= 2 0		
0	775	896
2	147	160
4	148	-158
6	57	-54
8	47	-45
10	45	46
12	27	-28
14	19	21
16*	0	-4
18	52	-48
20	36	-39
22*	0	2
24	51	44
K,L= 3 0		
2	24	-23
4	38	-35
6	295	270
8	48	-46
10	48	-48
12	11	3
14	12	-11
16*	0	12
18	51	-55
20*	0	-7
22*	0	-13
24	36	-31
K,L= 4 0		
0	212	-213
2	17	-8
4	105	-106
6	360	-323
8	70	-71
10	20	-24
12	69	-61
14	13	-9
16*	0	13
18	34	-36
20*	0	-6
22	35	37
24	11	15
K,L= 5 0		
2	38	-39
4	79	77
6	55	49
8	16	-20
10	14	13
12	41	-37
14	30	-33
16*	0	0
18	12	5
K,L= 6 0		
0	28	-31
2*	0	1
4	9	-5
6	82	-81
8	12	-11
10	13	16
12	82	-86
14	21	-20
16*	0	2
18	28	-32
K,L= 7 0		
2	15	22
4	21	22
6	27	25
8	19	17
10	48	54
12*	0	0
14	26	-30
16	12	17
K,L= 8 0		
0	126	131
2	37	36
4	18	24
6	85	87
8	61	64
10*	0	8
12	50	-58
14	17	-21
K,L= 9 0		
2	32	35
4	19	-27
6	67	69
8	52	48
10	27	32
12	20	22
K,L= 10 0		
0	38	38
2*	0	7
4	12	-17
6	61	64
8	57	60
10	15	-17
K,L= 11 0		
4	23	-22
6	41	41
8	45	37
K,L= 12 0		
0	36	-40
K,L= 1 1		
1	74	73
2	254	-245
3	308	308
4	620	665
5	533	562
6	178	178
7	62	63
8	8	9
9	11	12
10	60	-63
11	22	-25
12	11	17
13	65	-64
14	123	115
15	33	-34
16	25	28
17	31	-32
18*	0	7
19	21	23
20	37	-36
21*	0	8
22*	0	3
23	30	-28
24*	0	2
25	14	-13
26	16	-15
K,L= 2 1		
0	29	25
1	82	-84
2	123	-126
3	76	79
4	316	330
5	258	269
6	149	154
7	72	-74
8	69	-71
9	8	5
10	126	128
11	129	128
12	12	20
13	46	-47
14	38	41
15	11	-13
16	12	-13
17	27	25
18*	0	7
19	37	-39
20	47	46
21	25	-28
22	11	-11
K,L= 3 1		
1	211	-185
2	185	164
3	118	-109
4	68	70
5	154	144
6	91	89
7	72	-72
8	8	-15
9	102	-96
10	52	-59
11	25	-33
12	12	-13
13	33	-31
14	16	18
15	24	-25
16*	0	4
17*	0	0
18	32	-30
19	43	46
20	16	-20
21	11	15
22	16	-19
23*	0	-7
24	15	-15
K,L= 4 1		
0	134	-118
1	53	49
2	24	-27
3	16	18
4	87	87
5	59	61
6	31	35
7	47	-50
8	23	27
9	38	-38
10	70	64
11	50	48
12*	0	9
13	27	-29
14*	0	7
15*	0	-1
16*	0	-7
17*	0	4
18*	0	11
19	30	-31
20	23	25
21	12	-16
K,L= 5 1		
1	154	-136
2	143	130
3	64	-68
4	55	-55
5*	0	9
6*	0	-10
7	84	-81
8	47	43
9	86	-83
10	23	-29
11	26	-26
12	21	-20
13	18	-19
14*	0	-4
15	19	-20
16	24	-28
17*	0	0
18	29	-28
19	20	25
20	10	-8
21*	0	10
22	24	-23
K,L= 6 1		
0	129	-115
1	94	88
2	59	-59
3	15	18
4	57	-60
5	14	-18
6	34	-35
7*	0	0
8	54	52
9	33	-37
10*	0	-5
11*	0	-13
12	22	-28
K,L= 7 1		
2	15	-27
3	79	85
4	9	13
5	35	41
6*	0	1
7	13	-20
8	45	51
9*	0	-5
10*	0	7
11*	0	4
12*	0	5
13*	0	-9
14	24	26
15	12	-15
16	23	-27
17	19	-24
K,L= 8 1		
1	56	62
2	66	-68
3	32	35
4	46	-48
5*	0	4
6*	0	-8
7	20	29
8*	0	-4
9*	0	0
10*	0	13
11	12	6
12	12	-18
13	20	25
14*	0	8
15	20	21
K,L= 9 1		
1	32	34
2	64	-68
3	79	80
4*	0	1
5	25	27
6	37	40
7*	0	-9
8	12	20
9	11	8
10	16	17
11	16	17
12	21	21
K,L= 10 1		
0	14	20
1	25	27
2	25	-28
3	29	34
4*	0	0
5	21	26
6*	0	11
7	11	14
8	16	-21
9*	0	6
10	17	19
11	24	21
12	21	23
13*	0	8
14	14	15
K,L= 11 1		
2	25	-30
3*	0	2
4	15	-22
5*	0	-9
6	20	23
7*	0	-15
8*	0	-1
9*	0	-11
10*	0	10
11	18	18
K,L= 0 2		
0	60	-47
1	82	-77
2	187	181
3	160	163
4	91	94
5	28	-23
6	116	113
7	97	101
8	41	42
9	382	378
10	69	-67
11	147	140
12	66	63
13	35	33
14	56	-54
15	44	-42
16	51	-47
17*	0	3
18*	0	-1
19	48	44
20	19	-17
21*	0	-4
22*	0	1
23*	0	1
24	10	-11
K,L= 1 2		
1	13	11
2	33	34
3	170	171
4	68	72
5*	0	4
6	85	-84
7	10	-6
8	149	141
9	163	161
10	81	77
11	14	15
12	22	20
13	15	-12
14	17	17
15	72	67
16	24	-23
17	15	9
18	26	21
19*	0	-9
20*	0	1
21	9	11
K,L= 2 2		
0	35	34
1	100	-100
2	86	-81
3	85	84
4	33	-29
5	25	-24
6	33	-30
7	23	17
8	48	46
9	244	248
10	50	43
11	84	79
12	9	-5
13	21	-17
14	12	-5
15	65	-66
16*	0	2
17	14	-10
18*	0	-3
19	15	15
20*	0	4
21	20	-17
K,L= 3 2		
1	16	16
2	23	-18
3	195	177
4	70	-61
5	38	37
6	81	-80
7	21	-22
8	127	124
9	200	192
10	122	116
11	8	7
12	15	19
13	19	-17
14*	0	-8
15	112	109
16	32	-35
17	17	14
18	19	20
19	15	-8
20*	0	6
21	9	10
K,L= 4 2		
0	103	89
1	58	-56
2	158	-144
3	40	33
4	164	-146
5	9	-13
6	55	-53
7	41	-38
8	20	18
9	80	72
10	74	70
11*	0	5
12	63	-60
13	65	-64
14	36	37
15	74	-74
16	54	53
17	27	-25
18*	0	0
19	18	-18
20	16	11
21	31	-29
K,L= 5 2		
1	36	-33
2	79	-75
3	76	-71
4	157	-149
5	23	20
6	9	12
7	33	-32
8*	0	-13
9	17	16
10	20	16
11*	0	-8
12*	0	0
13*	0	3
14	57	-56
15	41	38
16	13	-17
17*	0	3
18	18	-20
19*	0	8
20*	0	11
21	13	-12
22	23	21
K,L= 6 2		
0	67	64
1	38	34
2*	0	8
3	36	33
4	74	-65
5	12	-19
6	11	-17
7*	0	4
8	34	35
9	33	34
10*	0	2
11*	0	-1
12*	0	-6
13	23	-23
14	14	11
15	23	-26
16	23	23
17	15	-12
18*	0	-3
19*	0	-3
20	14	-17
21	17	-17
K,L= 7 2		
1	51	-49
2	97	-95
3	136	-131
4	79	-74
5*	0	0
6	18	20
7	15	-17
8	14	-10
9	47	-49
10*	0	-6
11*	0	-8
12*	0	-5
13	10	8
14	21	-20
15	9	-2
16	12	-12
17*	0	5
18	14	-15
19	15	14
20	9	10
21	14	-18
K,L= 8 2		
0	36	33
1	67	64
2	57	58
3	50	50
4*	0	7
5*	0	-11
6*	0	-1
7	27	26
8*	0	5
9	34	34
10	10	-14
11*	0	10
12	24	18
13	13	14
14*	0	-6
15	8	9
16	9	-9
K,L= 9 2		
1	32	-28
2	44	-37
3	61	-57
4*	0	1
5*	0	7
6*	0	4
7*	0	5
8	31	32
9*	0	-2
10	14	15
11*	0	1
12*	0	5
13*	0	0
14	9	9
15	14	12
K,L= 10 2		
0	9	10
1	37	33
2*	0	1
3	37	34
4*	0	4
5*	0	2
6*	0	-7
7*	0	-1
8	19	-18
9*	0	5
10*	0	1
11	11	10
K,L= 11 2		
7	16	16
8	8	13
9	27	28
K,L= 1 3		
1	47	-50
2	89	-83
3	31	-31
4	229	205
5	190	-165
6	111	99
7	11	-10
8	30	-28
9	7	2
10	82	75
11	9	-12
12	63	59
13	24	22
14	25	24
15	16	14
16	41	39
17*	0	9
18*	0	-7
19	29	-29
20	24	-24
21	21	-18
22	9	13
23*	0	-10
24	7	11
K,L= 2 3		
0	190	181
1	62	64
2	131	129
3	84	79
4	99	-92
5	64	52
6	10	-2
7	113	112
8	73	73
9	33	34
10	21	8
11	20	-23
12	79	73
13	94	90
14	27	24
15	65	61
16	12	17
17	12	11
18	12	13
19	23	24
20	19	-21
21	10	9
22*	0	7
23*	0	-2
24	10	12
K,L= 3 3		
1	127	-107
2	121	-106
3	20	-20
4	86	84
5	60	-59
6	13	-16
7*	0	5
8	46	45
9*	0	10
10	109	-108
11	38	41
12	33	-32
13	70	64
14	92	86
15	40	41
16	46	-46
17	32	33
18	35	-36
19*	0	6
20	12	-17
K,L= 4 3		
0	191	154
1	45	37
2	21	21
3	55	48
4*	0	-4
5	22	-19
6	53	-51
7*	0	-1
8	21	-26
9	37	-40
10	58	62
11	75	-76
12	21	28
13	43	42
14	46	44
15	26	27
16*	0	5
17	12	11
18	23	-25
19	15	18
K,L= 5 3		
1	43	-39
2	43	-38
3*	0	-6
4*	0	4
5	11	19
6	20	28
7	13	21
8	20	28
9	13	16
10	130	-129
11	44	49
12	40	-39
13	47	48
14	79	75
15	21	26
16	43	-43
17	23	24
18	44	-45
19	15	18
K,L= 6 3		
0	15	20
1	11	-16
2	30	-30
3	11	14
4	12	17
5	25	-27
6	86	-90
7	92	-95
8	90	-89
9	75	-78
10	62	64
11	60	-60
12*	0	5
13	24	-28
14	36	34
15	11	-13
16	11	-17
17	13	14
18	45	-43
19*	0	2
20	8	9
21	6	-9
K,L= 7 3		
3	15	-16
4*	0	3
5	29	30
6	67	68
7	26	30
8*	0	-4
9	11	4
10	26	-27
11*	0	7
12*	0	9
13*	0	2
14	16	22
15	10	-9
16	10	13
17*	0	0
18	13	-16
K,L= 8 3		
0	12	-17
1	12	-14
2	12	-13
3*	0	10
4*	0	-9
5*	0	0
6	50	-53
7	55	-54
8	51	-49
9	30	-32
10	11	12
11	11	-12
12	27	31
13	10	-11
14	9	12
15*	0	2
16	14	-18
17	14	16
18	14	-16
K,L= 9 3		
3	22	-21
4	18	25
5*	0	0
6	30	32
7*	0	11
8*	0	-7
9*	0	-2
10	10	15
11	9	-15
12	9	13
13	16	-17
14	19	2
15	6	-12
16	22	18
K,L= 10 3		
0	10	14
1*	0	-8
2*	0	-2
3*	0	4
4	10	-17
5*	0	7
6*	0	1
7*	0	-1
8*	0	-6
9*	0	4
10*	0	3
11*	0	2
12	37	31
K,L= 11 3		
0	18	0
1	11	-21
2	11	-14
3	7	-13
4	10	8
K,L= 0 4		
0	175	-169
1	27	27
2	35	-35
3	9	8
4	19	-25
5	39	-35
6	193	-179
7	30	26
8*	0	1
9	36	34
10	32	30
11	14	-15
12	63	-57
13*	0	6
14*	0	9
15*	0	0
16	14	19
17	14	13
18	38	-42
19	41	40
20*	0	-11
21*	0	8
22*	0	-4
23	7	-8
24	15	-18
K,L= 1 4		
1	113	-94
2	20	14
3	18	21
4	9	14
5	32	33
6	113	103
7*	0	-1
8	14	16
9*	0	4
10	28	27
11*	0	-8
12	43	42
13	11	-13
14	30	27
15*	0	1
16	37	37
17*	0	2
18*	0	6
19*	0	8
20*	0	7
21*	0	8
22	8	11
K,L= 2 4		
0	218	-213
1	18	15
2	4	5
3*	0	9
4	25	-28
5	62	-55
6	94	-79
7	39	-35
8	15	16
9	18	19
10*	0	-2
11*	0	-4
12	49	46
13	31	-29
14	23	18
15	15	-16
16	11	12
17	15	16
18	12	3
19	33	32
K,L= 3 4		
1	120	-98
2*	0	3
3	24	27
4	35	35
5	66	64
6	61	59
7	25	24
8	20	20
9*	0	4
10*	0	-2
11	23	-25
12	41	39
13	42	-38
14	50	49
15*	0	-9
16	31	36
17	14	10
18	15	16
19	14	16
20	9	10
21	10	12
22	13	12
K,L= 4 4		
0	118	-93
1*	0	-2
2*	0	8
3	7	11
4	7	1
5	56	-53
6	46	51
7	87	-84
8	12	11
9	20	24
10	25	-25
11	13	14
12	170	145
13	64	-61
14	27	22
15	38	-36
16	14	-5
17	14	17
18	54	50
19	16	18
20	9	11
K,L= 5 4		
1	19	-24
2*	0	2
3*	0	-4
4*	0	8
5	65	67
6	105	-102
7	70	68
8*	0	-5
9*	0	5
10	64	-62
11	37	-36
12	40	-40
13	54	-51
14	19	21
15	13	-14
16	24	-26
17	15	14
18	16	19
19	9	11
K,L= 6 4		
0	11	3
1*	0	-2
2	13	-18
3*	0	7
4	23	27
5	38	-40
6	62	61
7	45	-42
8*	0	-14
9	33	36
10*	0	10
11	16	23
12	64	64
13	20	-24
14	10	9
15	17	-20
16	16	-12
17	11	10
18	24	23
19	10	11
20	11	11
K,L= 7 4		
3	16	-18
4	12	-11
5	43	44
6	94	-94
7	50	52
8	21	-27
9*	0	6
10	38	-39
11	36	-38
12	36	-36
13	42	-43
14*	0	-10
15*	0	-4
16	24	-20
17	13	13
18	12	13
K,L= 8 4		
2	21	-23
3*	0	-3
4	11	14
5	21	-22
6*	0	0
7	11	6
8*	0	-11
9	23	25
10	12	13
11	10	16
12	21	-23
13*	0	6
14	10	-6
K,L= 9 4		
5	10	14
6	10	-13
7	10	16
8	15	-18
9*	0	3
10*	0	11
11	24	-22
12	25	5
13	23	-21
K,L= 10 4		
0	37	-34
1*	0	7
2	13	-14
3*	0	-5
4	9	-8
5	8	-12
6	24	-20
K,L= 11 4		
2	11	-13
K,L= 1 5		
1	33	-33
2*	0	-1
3	21	-25
4	10	-15
5	43	-42
6*	0	-7
7	45	47
8	41	-41
9*	0	-12
10	96	-95
11	33	-23
12	15	-18
13*	0	-13
14	58	58
15	32	-35
K,L= 2 5		
0	9	-11
1	51	55
2	81	-79
3	13	17
4	26	-20
5	54	-56
6	27	-26
7	72	73
8	87	-88
9	104	99
10*	0	-7
11	17	20
12*	0	0
13	46	48
14*	0	-8
15*	0	11
16	14	-17
17*	0	-5
18*	0	-5
19	24	25
20	11	12
21	9	10
K,L= 3 5		
2	17	19
3	13	-10
4	53	-50
5	73	-70
6*	0	1
7	47	49
8	88	-86
9	59	59
10	47	-41

TABLE 5. Continued

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
11	13	-16	6*	0	-12	1	47	45	10	38	-42	K,L=	3	6	K,L=	6	6	9*	0	-4	K,L=	0	8	1	24	-31
12*	0	-2	7	40	44	2	34	-32	11	38	38	3	89	-82	4	14	17	10	23	-22	0	57	62	2*	0	2
13*	0	-5	8	52	-53	3	13	-15	12*	0	9	4	67	70	5*	0	13	K,L=	3	7	1*	0	-22	3*	0	-7
14*	0	2	9	52	55	4	14	17	13	34	-34	5	47	-47	6*	0	9	1	35	39	2*	0	-13	4*	0	-5
15	17	21	10*	0	0	5	13	-16	14	29	-28	6*	0	-10	7*	0	0	2*	0	8	3*	0	3	5*	0	5
16	30	34	11*	0	-11	6	13	-14	15	32	-26	7*	0	2	8*	0	-4	3*	0	-4	4	41	43	6	13	17
17	20	22	12*	0	1	7	13	16	16	27	-27	8*	0	3	9	18	-19	4*	0	11	5	62	67	7*	0	1
K,L=	4	5	13*	0	4	K,L=	8	5	K,L=	1	6	9	59	-61	K,L=	7	6	5	15	-29	6	68	73	8	12	-13
0	15	17	14*	0	-9	0	44	46	3	76	-73	10	31	37	1	12	17	6	15	-10	7*	0	27	K,L=	4	8
1*	0	-6	15	33	33	1	56	-54	4	57	59	11*	0	-15	2	21	26	7	26	-28	8*	0	1	0	48	-50
2	20	23	16	28	29	2	34	39	5	45	-42	12*	0	4	3	76	79	K,L=	4	7	9	18	-22	1*	0	18
3	37	-35	17	22	20	3	24	-32	6*	0	-13	13*	0	5	4*	0	2	4	19	-18	10*	0	0	2*	0	-9
4	12	-14	18	10	8	K,L=	9	5	7*	0	0	14*	0	4	5	12	14	5	30	31	11*	0	4	3*	0	5
5	63	-56	19	12	-12	0	17	0	8*	0	14	15	13	-17	6*	0	5	K,L=	5	7	12	15	-19	4*	0	8
6*	0	-7	K,L=	6	5	1	21	17	9	33	-36	K,L=	4	6	7*	0	2	4	13	19	13	14	13	5*	0	-2
7	28	27	0	54	53	2	20	-23	10	27	29	2	19	-25	8*	0	-6	5	13	-19	14*	0	-6	6	15	-14
8	24	-30	1	76	-77	3*	0	-24	K,L=	2	6	3	52	-53	9*	0	4	6*	0	0	15	12	16	7	10	17
9	60	56	2	79	81	4*	0	-4	0	52	-48	4	14	19	10	17	-22	7	18	-27	K,L=	1	8	K,L=	6	8
10	24	-25	3	60	-62	5*	0	-6	1*	0	4	5	14	-17	11	9	6	8	12	-16	1	14	-20	0	16	-18
11*	0	0	4*	0	6	6	10	3	2*	0	14	6	19	22	K,L=	1	7	9*	0	0	K,L=	2	8	K,L=	1	9
12	20	21	5*	0	-11	7*	0	-12	3	74	-76	7	14	14	1	131	130	10	11	15	0	12	5	5	10	18
13	14	14	6*	0	5	8	23	9	4	66	68	8	24	-28	2	81	83	11*	0	-11	1*	0	-1	6*	0	-2
14	19	-22	7	23	-27	9	15	-18	5	59	-56	9	24	-23	3*	0	-3	12*	0	7	2*	0	-10	7	9	-13
15*	0	-11	8	23	29	K,L=	0	6	6*	0	12	K,L=	5	6	4	35	-40	13	9	-14	3*	0	4	8	29	31
16	18	-20	9*	0	-2	0	103	-99	7*	0	0	1	33	33	K,L=	2	7	K,L=	6	7	4	25	26	9*	0	8
17	17	-17	10	14	-13	1*	0	15	8	24	-24	2	29	34	0	70	-73	0	28	33	5	35	35	10	27	34
18	10	-5	11	14	-15	2	72	71	9*	0	-3	3	29	39	1*	0	-19	1*	0	11	6	36	34	K,L=	2	9
19	9	12	12	13	16	3	73	-73	10	18	-24	4*	0	3	2*	0	-8	2*	0	8	7	21	22	7	11	-13
K,L=	5	5	13	13	-17	4	94	97	11	13	16	5*	0	5	3*	0	-6	3*	0	5	8*	0	-1	K,L=	3	9
1	38	35	14	12	-15	5	75	-67	12*	0	0	6*	0	5	4	39	-43	4*	0	10	9	18	-18	2	17	8
2*	0	-7	15	31	-26	6*	0	8	13	12	-15	7*	0	4	5	37	43	5*	0	5	10*	0	-8	K,L=	4	9
3*	0	2	16	18	-7	7	34	-13	14	12	-13	8	14	-18	6	36	-41	6	29	30	11*	0	-3	3	10	-13
4*	0	-8	17	23	-19	8*	0	-10	15	14	-14	9	14	-18	7*	0	16	K,L=	7	7	12	17	-17			
5	52	-52	K,L=	7	5	9*	0	10	16	20	-18	10	13	-12	8*	0	16	10	11	13	K,L=	3	8			

TABLE 6(a). BOND LENGTHS WITH THEIR e. s. d.' s

	Length (Å)	e.s.d. (Å)
N(1)-C(1)	1.328	0.007
N(1)-C(2)	1.364	0.006
C(1)-C(2)	1.395	0.007
C(2)-C(3)	1.463	0.007
C(3)-C(4)	1.330	0.007
C(4)-C(5)	1.469	0.007
C(5)-C(6)	1.412	0.007
C(5)-C(7)	1.405	0.007
C(6)-C(8)	1.389	0.008
C(7)-C(9)	1.389	0.008
C(8)-C(10)	1.394	0.008
C(9)-C(10)	1.394	0.008
C(1)-H(1)	1.050	0.059
C(3)-H(3)	1.100	0.058
C(4)-H(4)	1.083	0.059
C(6)-H(6)	1.083	0.058
C(7)-H(7)	1.082	0.058
C(8)-H(8)	1.062	0.058
C(9)-H(9)	1.087	0.057
C(10)-H(10)	1.061	0.056

TABLE 6 (b). BOND ANGLES WITH THEIR e. s. d.' s

	Angle(Å)	e.s.d.(Å)
C(2)-N(1)-C(1)	115.8	0.5
C(2)-C(1)-N(1)	124.1	0.6
N(1)-C(2)-C(1)	120.2	0.4
C(1)-C(2)-C(3)	120.8	0.4
N(1)-C(2)-C(3)	119.0	0.4
C(2)-C(3)-C(4)	126.0	0.5
C(3)-C(4)-C(5)	127.0	0.5
C(4)-C(5)-C(7)	122.7	0.4
C(4)-C(5)-C(6)	119.6	0.4
C(6)-C(5)-C(7)	117.7	0.4
C(5)-C(6)-C(8)	120.7	0.5
C(5)-C(7)-C(9)	121.5	0.5
C(6)-C(8)-C(10)	120.6	0.5
C(7)-C(9)-C(10)	120.1	0.5
C(8)-C(10)-C(9)	119.4	0.5
C(2)-C(1)-H(1)	117.0	3.2
C(2)-C(3)-H(3)	116.6	3.1
C(4)-C(3)-H(3)	117.4	3.1
C(3)-C(4)-H(4)	116.7	3.1
C(5)-C(4)-H(4)	116.4	3.1
C(5)-C(6)-H(6)	118.8	3.1
C(8)-C(6)-H(6)	120.5	3.1
C(5)-C(7)-H(7)	118.6	3.1
C(9)-C(7)-H(7)	120.0	3.1
C(6)-C(8)-H(8)	118.7	3.2
C(10)-C(8)-H(8)	120.7	3.2
C(7)-C(9)-H(9)	120.6	3.0
C(10)-C(9)-H(9)	119.3	3.0
C(8)-C(10)-H(10)	120.0	3.1
C(9)-C(10)-H(10)	120.5	3.1

118.2° in diethylstilbestrol,[7] 118.2° in 1.8-diphenyl-1,3,5,7-octatetraene,[8] 118.2° in chalcone,[9] 117° in *p*-methoxychalcone[10] and 118.4° in *p*-coumaric acid.[11] Such a decrease may be interpreted as being due to interatomic repulsion induced by the substituent.

In the pyrazine ring there are two kinds of C–N bonds. The C–N bond adjacent to the substituent (C(2)–N(1)=1.346 Å) is longer than the other (C(1)′–N(1)=1.328 Å). Similar differences are observed in the substituted pyridine ring: 1.37 and 1.35 Å for 2,2-bipyridine,[12] and 1.362 and 1.337 Å for 2-(2-pyridylmethyldithio)benzoic acid.[13] The C–C bond length of the pyrazine ring, 1.395 Å, is compared to that of the benzene ring. These bond lengths are different

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[7] a) C. M. Weeks, A. Cooper, and D. A. Norton, *ibid.*, **B26**, 429 (1970). b) I. E. Smiley and M. G. Rossmann, *Chem. Commun.*, **1969** 198.

[8] W. Drenth and E. H. Wiebenga, *Acta Crystallogr.*, **8**, 755 (1955).

[9] D. Rabinovich, *J. Chem. Soc.*, *B*, **1970**, 11.

[10] D. Rabinovich and G. M. J. Schmidt, *ibid.*, *B*, **1970**, 6.

[11] H. Utsumi, K. Fujii, H. Irie, A. Furusaki, and I. Nitta, *Nippon Kagaku Zasshi*, **91**, 439 (1970).

[12] L. L. Merritt, Jr., and E. D. Schroeder, *Acta Crystallogr.*, **9**, 801 (1956).

[13] J. Karl, I. L. Karl, and D. Mitchell, *ibid.*, **B25**, 866 (1969).

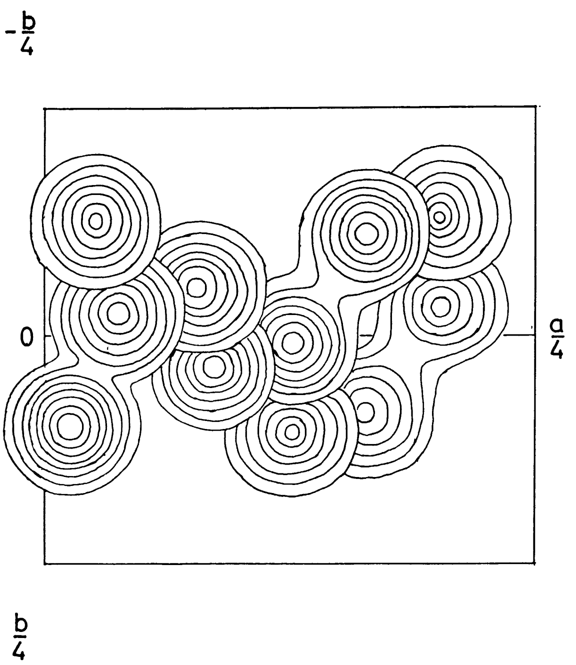

Fig. 2. Composite electron density diagram of sections parallel to (001). Contours are at intervals of 1.0 e.Å^{-3}, starting at 1.0 e.Å^{-3}.

from those of pyrazine itself;[14] C–N and C–C are 1.334 and 1.378 Å respectively. The C–N–C bond angle, 115.8°, is similar to that of pyrazine, 115.7°, and somewhat smaller than that in substituted pyridine: 116.7° in 1-phenyl-2-(2-pyridyl)ethanedione-1,2,[15] 118.5° in 2-(2-pyridylmethyldithio)benzoic acid,[13] and 120.6° in *cis*-β-bromo-β-(2-pyridyl)styrene.[16]

The bond lengths of C(2)–C(3) (1.463 Å), C(4)–C(5) (1.469 Å), and C(3)–C(4) (1.330 Å) are reasonable as those in a conjugated system; for example, in 1,8-diphenyl-1,3,5,7–octatetraene[8] the single bond length is 1.468 Å and the double bond length is 1.350 Å. The C(2)–C(3)–C(4) angle (126.0°) and the C(3)–C(4)–C(5) angle (127.0°) are considerably greater than 120°. Similar results have been reported for di-substituted ethylene: 128° for stilbene,[17] 126.8° for 1,8–diphenyl-1,3,5,7-octatetraene,[8] 127.6° for chalcone,[9] 127.2° for *p*-methoxychalcone,[10] 125.8° for *p*-coumaric acid,[11] 122.2° for diethylstilbestrol,[7] and 122.7° for 1,2-di-2-pyridylethenediol-1,2.[18]

It is noteworthy that the bond angles of nearly planar styryl groups (in the above-mentioned substances as well as the present compound) show very common features. The angles of C(3)–C(4)–C(5), C(4)–C(5)–C(7), and C(6)–C(5)–C(7) are 127°, 123°, and 118° respectively within a range of about one degree.

The equations of the average planes were evaluated by the method of least-squares. None of the hydrogen atoms were include because of the large standard deviations in their atomic coordinates. The equations are:

$$0.78278x + 0.41637y + 0.46215z - 3.53357 = 0 \qquad (1)$$

for the plane of all eleven atoms;

$$0.75315x + 0.48099y + 0.44879z - 3.39271 = 0 \qquad (2)$$

for the plane of the benzene ring;

$$0.81100x + 0.28777y + 0.50939z - 3.89936 = 0 \qquad (3)$$

for the plane of the pyrazine ring, and

$$0.77506x + 0.43947y + 0.45404z - 3.46952 = 0 \qquad (4)$$

TABLE 7. DISPLACEMENTS (Å) FROM THE AVERAGE PLANES

	plane (1)	plane (2)	plane (3)[a]	plane (4)
N(1)	−0.1813		−0.0059	−0.2119[b]
C(1)	0.1532		−0.0062	0.1809[b]
C(2)	−0.0010		0.0061	−0.0012
C(3)	−0.0018	0.0077[b]	0.0018[b]	0.0012
C(4)	0.0234	−0.0278[b]	0.1763[b]	0.0012
C(5)	0.0185	−0.0078		−0.0012
C(6)	0.1068	0.0071		0.0579[b]
C(7)	−0.0652	0.0034		−0.0544[b]
C(8)	0.0763	−0.0019		
C(9)	−0.0880	0.0018		
C(10)	−0.0188	−0.0026		

a) In addition to these three atoms, the centre of symmetry(0,0,1) was included in the plane evaluation.
b) These atoms were not included in the plane evaluation.

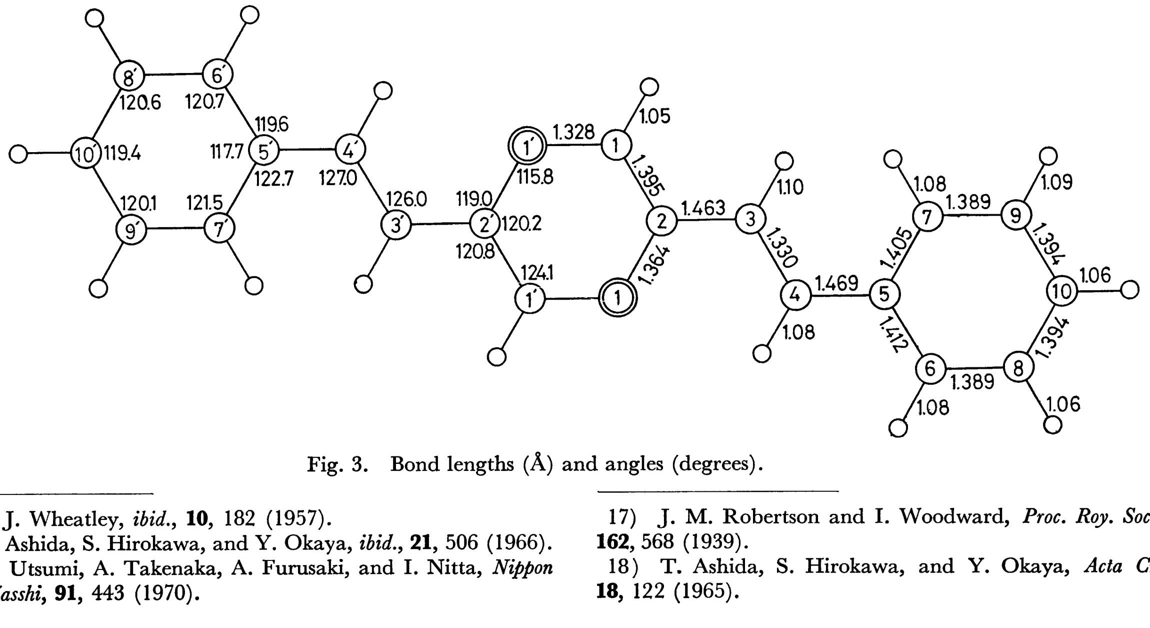

Fig. 3. Bond lengths (Å) and angles (degrees).

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14) P. J. Wheatley, *ibid.*, **10**, 182 (1957).

15) T. Ashida, S. Hirokawa, and Y. Okaya, *ibid.*, **21**, 506 (1966).

16) H. Utsumi, A. Takenaka, A. Furusaki, and I. Nitta, *Nippon Kagaku Zasshi*, **91**, 443 (1970).

17) J. M. Robertson and I. Woodward, *Proc. Roy. Soc., Ser. A*, **162**, 568 (1939).

18) T. Ashida, S. Hirokawa, and Y. Okaya, *Acta Crystallogr.*, **18**, 122 (1965).

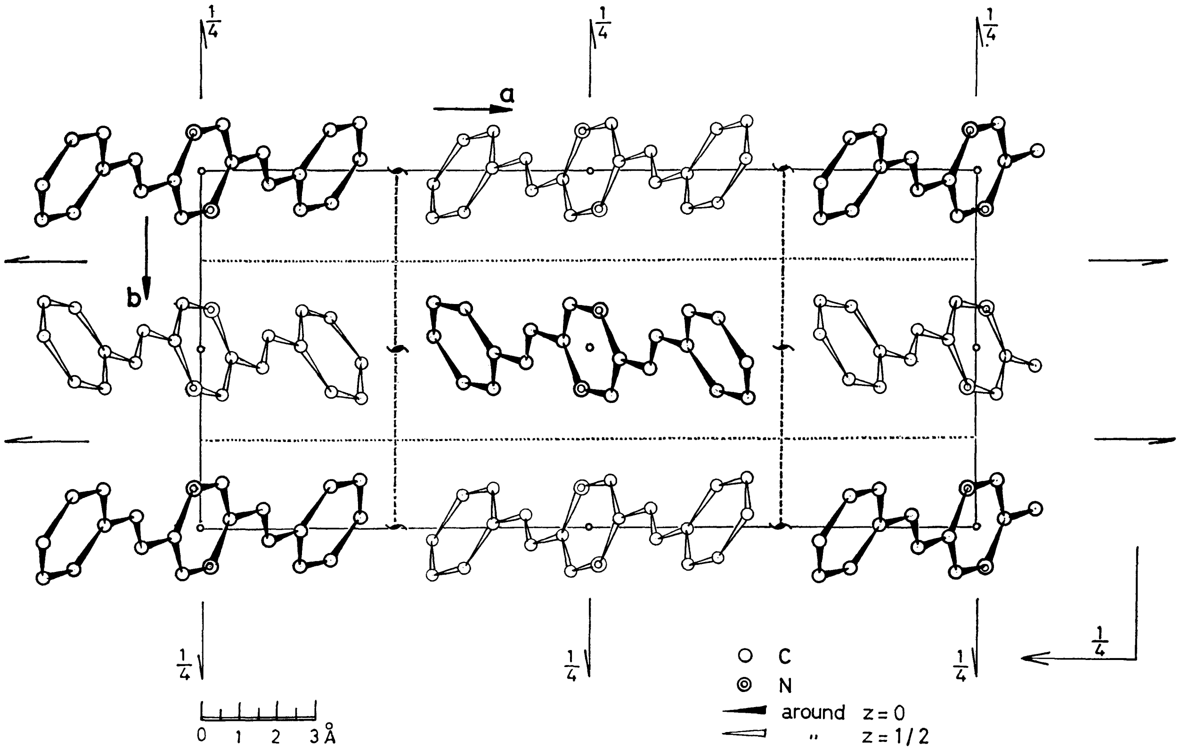

Fig. 4. The crystal structure viewed along the *c*-axis.

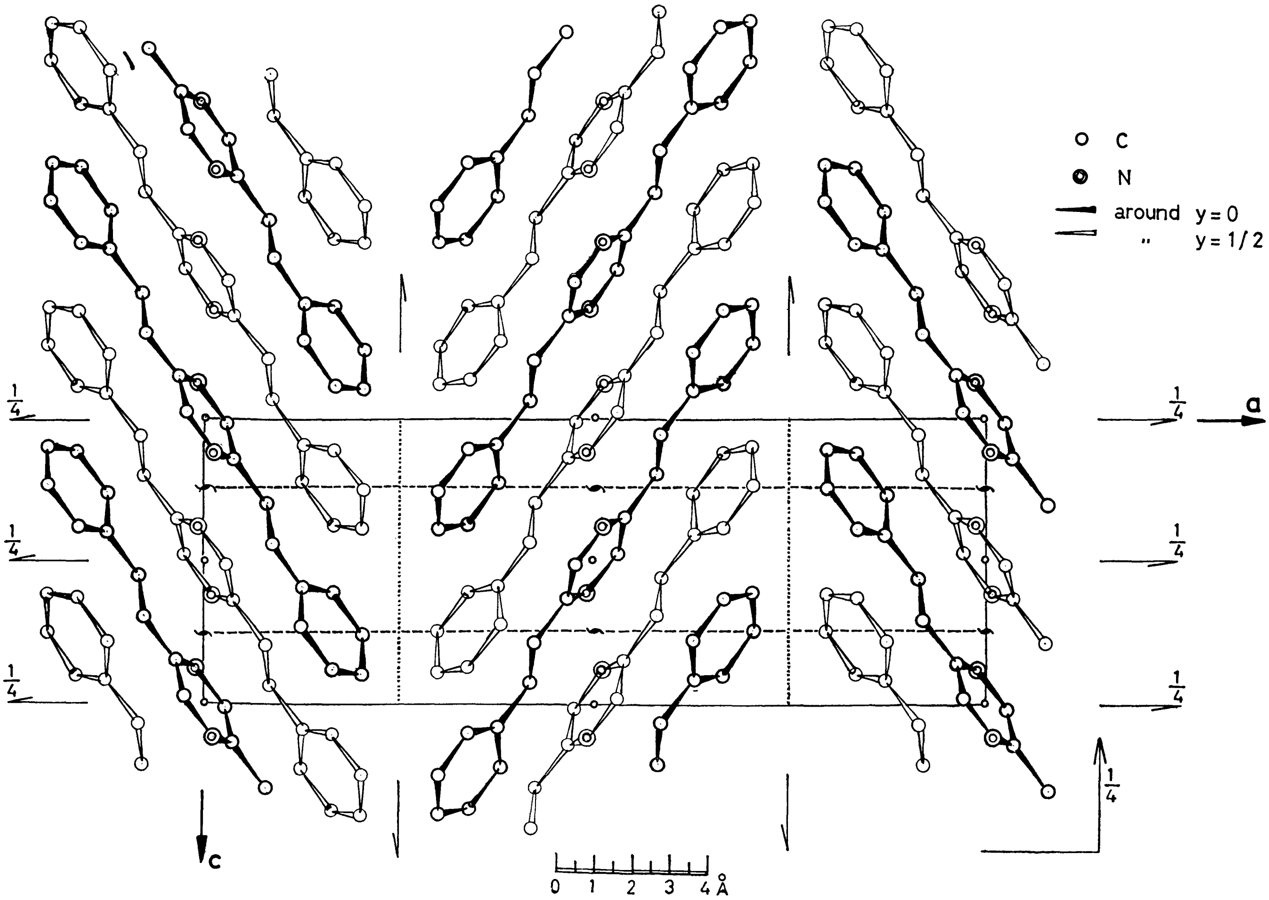

Fig. 5. The crystal structure viewed along the *b*-axis.

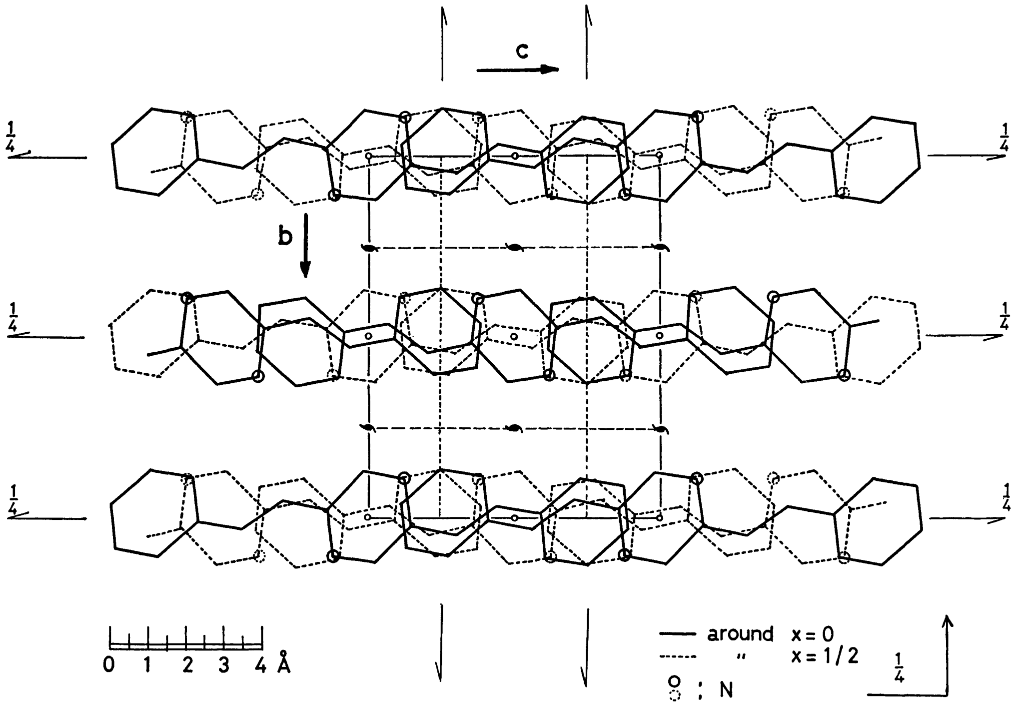

Fig. 6. The crystal structure viewed along the *a*-axis.

for the plane through the atoms C(2), C(3), C(4), and C(5), where *x*, *y*, and *z* are in Å.

The displacement of the atoms from each plane are shown in Table 7. The maximum deviations are 0.008 Å for the plane (2), 0.006 Å for the plane (3), and 0.001 Å for the plane (4). Therefore, these three groups of the atoms are planar.

However, the molecule as a whole is not planar, as may be seen from Table 7. The benzene ring rotates by 2.61° about the bond C(4)–C(5), and the pyrazine ring rotates by 9.42° about C(2)–C(3) in the opposite direction. Therefore, the dihedral angle between the planes (2) and (3) is 12.09°. The rotation about C(4)–C(5) may be due to a repulsion between the

Table 8. Intermolecular distances less than 4.0 Å

Atom in molecule 1	Atom	in molecule	Distance (Å)
C(6)	C(1)	2	3.775
C(6)	C(2)	2	3.893
C(6)	N(1)	2	3.856
C(8)	C(1)	2	3.688
C(8)	C(2)	2	3.520
C(8)	C(3)	2	3.945
C(8)	N(1)	2	3.715
C(10)	C(1)	2	3.905
C(10)	C(2)	2	3.963
C(1)	C(6)′	2	3.692
C(2)	C(5)′	2	3.932
C(2)	C(6)′	2	3.590
C(3)	C(4)′	2	3.939
C(4)	C(3)′	2	3.939
C(4)	C(4)′	2	3.702
C(5)	C(2)′	2	3.932
C(5)	N(1)′	2	3.755
C(6)	C(1)′	2	3.692
C(6)	C(2)′	2	3.590
C(6)	N(1)′	2	3.675
C(5)	C(10)	3	3.880
C(7)	C(8)	3	3.980
C(7)	C(10)	3	3.515
C(9)	C(10)	3	3.773
C(3)	C(1)	4	3.706
C(7)	C(1)	4	3.869
C(7)	C(3)	4	3.981
C(9)	C(7)	4	3.740
C(10)	C(7)	4	3.880
C(3)	C(3)	4	5.414[a]
C(1)	N(1)′	4	3.837
C(3)	N(1)′	4	3.807
C(6)	C(4)	5	3.912
C(6)	N(1)	5	3.719
C(4)	C(4)	5	5.652[a]
N(1)	C(1)′	5	3.837
N(1)	C(3)′	5	3.807

a) Listed for investigating the distances between double bonds.

Molecule	General coordinate
1	x, y, z
2	$x, y, -1.0+z$
3	$0.5-x, -y, 0.5+z$
4	$x, -0.5-y, -0.5+z$
5	$x, 0.5-y, -0.5+z$

hydrogen atoms attached to C(3) and C(7). The interatomic distance between these hydrogen atoms is 2.04 Å (e.s.d.=0.08 Å). Although, for the rotation about C(2)–C(3), no such repulsion is operative because of the absence of any hydrogen attached to the N atom, the rotation about C(2)–C(3) is larger than that about C(4)–C(5). This may be interpreted in terms of some intermolecular interactions.

Crystal Structure. The arrangements of molecules in the crystal viewed along the *c*-, *b*-, and *a*-axes are shown in Fig. 4, 5, and 6 respectively. Intermolecular distances less than 4.0 Å are listed in Table 8. No unusual short approaches are observed.

The molecules are oriented in such a way that their long axes are nearly perpendicular to the *b*-axis, as may be seen in Figs. 4 and 6. This arrangement can well explain the UV dichroism; the absorption parallel to the *c*-axis is ten times as strong as that parallel to the *b*-axis when measured on (100).[19]

The molecules spaced by the *c*-translation are also related by the centre of symmetry, the corresponding planar parts in these molecules being parallel to each other. As the long axis of the molecules makes an angle of about 30° to the *c*-axis, the molecules are piled up infinitely plane-to-plane, sliding in the direction of the long axis by half a molecule, as may be seen in Fig. 7.

The ethylenic double bonds, which are antiparallel to each other, approach to a distance of 3.939 Å from each other. This intermolecular distance between ethylenic double bonds is the shortest, while the second shortest contact of the same kind is 5.417 Å found between the molecules which are related by the *b*-glide plane. It is most probable that the double bonds related by the centre of symmetry react to form a a cyclobutane ring by photo-irradiation,[20] resulting in a linear ploymer. Thus, polymer chains should grow in the direction of the *c*-axis. This is confirmed by X-ray-crystallographic[21] and electron-microscopic[22] studies of the polymer thus obtained.

In order to investigate the intermolecular contacts involving the double bonds, the molecule 2 is projected on the best plane of the moecule 1 in Fig. 7. The benzene ring in one molecule overlaps with the pyrazine ring in the other molecule. This type of parallel stacking of the aromatic rings has been observed in several other compounds. In the crystals of 1-phenyl-(2-pyridyl)ethanedione-1,2[15] and 2,2-pyridyl,[23] there are parallel pairs between the same aromatic rings and the perpendicular distances range from 3.49 to 3.80 Å. In the present crystal there are close contacts between unlike rings, with a plane-to-plane distance of 3.52 Å. Similar contacts are found in 2-(2-pyridylmethyldithio)benzoic acid. The UV spectrum of DSP in the crystalline state is different from that in solution, the former having a shoulder on the side of the longer wavelength[19]. The fact indicates that there is some kind of intermolecular interaction. As the short contacts are observed only between the parallel rings, it may be that the interaction of the overlapping part in Fig. 7, mainly determines the packing of the molecules in the crystal.

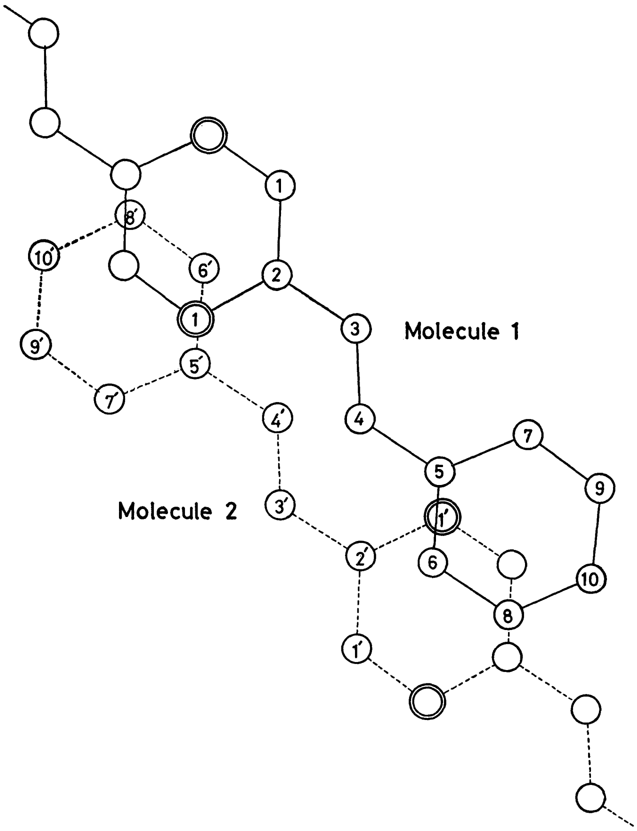

Fig. 7. The overlapping of the molecules viewed along the normal of the average plane of the reference molecule.

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[19] T. Tamaki, Y. Suzuki, and M. Hasegawa, Paper presented at the 19th Annual meeting of the Society of Polymer Science, Japan, Tokyo, May, 1970, p. 108.

[20] G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 2014.

[21] H. Nakanishi, M. Hasegawa, Y. Sasada, and H. Shimanouchi, Paper presented at the 19th Annual meeting of the Society of Polymer Science, Japan, Tokyo, May, 1970, p. 337 and to be published.

[22] H. Nakanishi, M. Nakano, and M. Hasegawa, *J. Polymer Sci.*, **B8**, 755 (1970).

[23] a) S. Hirokawa and T. Ashida, *Acta Crystallogr.*, **14**, 774 (1961). b) T. Ashida and S. Hirokawa, *ibid.*, **B26**, 454 (1970).