The Crystal and Molecular Structure of Two Forms of 1,3-Diphenyl-5-(p-chlorophenyl)-2-pyrazoline

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The title compound crystallizes in two forms, both belonging to the monoclinic system, space group $P2_1/c$. The unit-cell parameters are: α form, $a = 11.365$ (3), $b = 13.854$ (3), $c = 12.026$ (4) Å, $\beta = 112.26$ (3)°: β form, $a = 18.836$ (4), $b = 5.494$ (3), $c = 16.569$ (4) Å, $\beta = 96.38$ (3)°. Three-dimensional X-ray analyses of both forms were carried out. Final conventional R values were 0.072 for 2785 non-zero reflexions (α form), and 0.090 for 1987 non-zero reflexions (β form). The two phenyl groups are conjugated with the pyrazoline ring to a lesser degree than in 1,3-diphenyl-2-pyrazoline. The bulky p-chlorophenyl substituent may be a cause for the non-planarity of the diphenylpyrazoline moiety. The main difference in the molecular structures of the two forms is observed in the angle made by the p-chlorophenyl group with the pyrazoline ring in the crystal. The dihedral angles are 63.5 (4) and 80.1 (3)° for α and β forms respectively. The flexibility of this angle may account for the glass-forming ability of the title compound.

Introduction

It has been observed that 1,3-diphenyl-5-(p-chlorophenyl)-2-pyrazoline (abbreviated as Cl-PDPP hereafter) forms a very stable glass around room temperature with supercooling, and that large single crystals can be grown by a zone-refining method (Kato, Yamamoto, Shirota, Yokoyama & Mikawa, 1974). This compound shows high photoconductivity not only in the glassy state but also in the crystalline state. Therefore, this is considered to be a good model compound for comparison of the photoconductive properties in the amorphous and crystalline states. In order to investigate the effect of structure on the photoconductive properties, a three-dimensional X-ray structure analysis of this compound in the crystalline state was undertaken.

The crystal structure of diphenyl-2-pyrazoline (abbreviated as DPP hereafter) has been reported (Duffin, 1968), and the degree of conjugation and the extent of coplanarity of the three rings in the molecule has been fully discussed. It is of interest to study the effect of the bulky p-chlorophenyl substituent on the molecular structure. In the course of a preliminary study on recrystallization, and X-ray work, the presence of two crystalline forms had been observed, which also prompted this study.

Experimental

In order to obtain suitable crystals for X-ray work, many attempts at recrystallization were carried out with various solvents. Needle crystals were easily ob-

tained by ordinary evaporation of ethanol, n-hexane, or xylene solutions. When an n-hexane solution was evaporated slowly in a desiccator, however, some polyhedral crystals were obtained simultaneously with needle ones. Tentatively, we denote the polyhedral type of crystals α form, and needle crystals β form. The crystal data of both forms are listed in Table 1.

The measurement of intensity data from both crystals was carried out on a Rigaku automated single-crystal diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The θ–2θ scan technique was applied. The details of the experimental conditions were modified slightly according to the quality of the crystal

Table 1. *Crystal data and details of experimental conditions*

$C_{21}H_{17}ClN_2$, FW 332.8, monoclinic, $P2_1/c$.

	α Form	β Form
a (Å)	11.365 (3)	18.836 (4)
b (Å)	13.854 (3)	5.494 (3)
c (Å)	12.026 (4)	16.569 (4)
β (°)	112.26 (3)	96.38 (3)
U (Å³)	1752.3 (9)	1704.0 (9)
D_m (g cm⁻³)	1.27	1.30
D_c (g cm⁻³)	1.26	1.30
Z	4	4
μ for Mo $K\alpha$ (cm⁻¹)	2.20	2.25
Scan speed in 2θ (° min⁻¹)	4	2
$2\theta_{max}$ (°)	54	50
Scan range in θ (°)	$1.0 + 0.35 \tan \theta$	$0.9 + 0.35 \tan \theta$
Background (s)	7.5	10
Total number of reflexions	3847	3020
Number of non-zero reflexions	2785	1987

used in each case, but are mostly as summarized in Table 1. Lorentz and polarization corrections were applied, whereas the correction for absorption was ignored [μ(Mo $K\alpha$) = 2·20 and 2·25 cm^{-1}], which might limit the accuracy of the present analysis.

Structure determination

α Form

The structure was solved by the direct method with *MULTAN* (Germain, Main & Woolfson, 1971). An E map corresponding to the set of phases with the largest 'figure of merit' gave the locations of all non-hydrogen atoms. Structure refinement was carried out by the method of block-diagonal least squares (*HBLS* V program, Ashida, 1973). After several cycles of isotropic refinement, followed by anisotropic cycles, a difference Fourier map indicated the positions of all the H atoms. Several cycles of refinement including isotropic H atoms were carried out with the following weighting scheme: $w = 1/(\sigma^2 + a|F_o| + b|F_o|^2)$ for $|F_o| > 0$ and $w = FWT$ for $|F_o| = 0$, where σ denotes the deviation due to counting statistics, and values of a, b and FWT were adjusted so that average $w|\Delta F|^2$ values for the whole range of $|F_o|$ were similar. These values were $a = -0·01592$, $b = 0·00199$ and $FWT = 0·50172$. The atomic scattering factors for Cl, C and N were those given in *International Tables for X-ray Crystallography* (1974), and for H from Stewart, Davidson & Simpson (1965). The final conventional R value was 0·072 for 2785 non-zero reflexions (0·118 for all 3847 reflexions).

β Form

The structure was established by the heavy-atom method. Only one peak with $v = 0$ was found along the Harker line $(0,v,\frac{1}{2})$ in the Patterson map, which implied a y coordinate of Cl of around $\frac{1}{4}$ in space group $P2_1/c$. Therefore it was impossible to interpret the Patterson map uniquely to give the location of the Cl atom. Several trial structure factor–Fourier map calculations were carried out, one of which gave the correct structure. The refinement of the structure model was carried out in a similar way to the α form with non-zero reflexions. The final R value was 0·090 for 1987 non-zero reflexions. The coefficients in the weighting scheme mentioned above were: $a = 0·02457$ and $b = 0·00044$.

Final atomic parameters are listed in Tables 2, 3, 4 and 5.*

Table 2. *Atomic parameters of the heavy atoms in the α form, with their e.s.d.'s in parentheses*

Positional parameters are in fractions of cell edges ($\times 10^4$) and thermal parameters ($\times 10^4$) are in the form:
$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	9352·8 (9)	263·4 (6)	2296·2 (8)	164 (2)	639 (5)	169 (2)	7 (2)	110 (2)	55 (2)
N(1)	6661 (2)	4738 (2)	1500 (2)	109 (3)	67 (2)	103 (3)	−5 (3)	130 (4)	3 (3)
N(2)	7003 (2)	5668 (2)	1309 (2)	98 (3)	69 (2)	89 (2)	1 (3)	98 (4)	2 (3)
C(3)	7474 (3)	5641 (2)	494 (3)	73 (3)	66 (2)	70 (2)	5 (4)	54 (4)	2 (3)
C(4)	7487 (3)	4650 (2)	−2 (3)	110 (3)	66 (2)	84 (3)	6 (4)	91 (5)	3 (4)
C(5)	6719 (3)	4057 (2)	575 (3)	84 (3)	70 (2)	78 (3)	−4 (4)	60 (4)	−3 (4)
C(11)	5824 (3)	4637 (2)	2096 (3)	77 (3)	85 (2)	75 (3)	19 (4)	65 (4)	27 (4)
C(12)	5195 (3)	3767 (3)	2067 (3)	88 (3)	84 (2)	97 (3)	6 (4)	69 (5)	36 (4)
C(13)	4390 (3)	3676 (3)	2693 (3)	88 (3)	113 (3)	106 (3)	−7 (5)	76 (5)	69 (5)
C(14)	4208 (3)	4435 (3)	3345 (3)	109 (4)	145 (4)	99 (3)	−11 (6)	114 (5)	41 (5)
C(15)	4824 (3)	5293 (3)	3376 (3)	129 (4)	134 (4)	97 (3)	8 (6)	128 (6)	−12 (5)
C(16)	5632 (3)	5399 (3)	2757 (3)	115 (3)	97 (3)	86 (3)	−5 (5)	105 (5)	−2 (4)
C(31)	7970 (3)	6507 (2)	124 (3)	85 (3)	69 (2)	72 (3)	−2 (4)	65 (4)	1 (3)
C(32)	7765 (3)	7422 (2)	488 (3)	129 (4)	70 (2)	121 (3)	4 (4)	137 (6)	−1 (4)
C(33)	8190 (4)	8229 (3)	90 (4)	156 (4)	64 (2)	166 (4)	−2 (5)	157 (7)	9 (5)
C(34)	8854 (3)	8142 (3)	−657 (4)	135 (4)	83 (3)	152 (4)	−16 (5)	134 (7)	58 (5)
C(35)	9078 (3)	7247 (3)	−1005 (3)	122 (4)	98 (3)	109 (3)	−19 (5)	130 (6)	23 (5)
C(36)	8644 (3)	6428 (2)	−622 (3)	106 (3)	75 (2)	88 (3)	−12 (4)	98 (5)	−4 (4)
C(51)	7327 (3)	3099 (2)	1054 (3)	82 (3)	62 (2)	80 (3)	−19 (4)	63 (4)	2 (4)
C(52)	7138 (3)	2325 (2)	268 (3)	116 (3)	67 (2)	79 (3)	−25 (4)	35 (5)	−3 (4)
C(53)	7742 (3)	1457 (2)	641 (3)	144 (4)	54 (2)	108 (3)	−38 (4)	77 (6)	−21 (4)
C(54)	8547 (3)	1353 (2)	1827 (3)	103 (3)	61 (2)	106 (3)	−23 (4)	86 (5)	30 (4)
C(55)	8735 (3)	2095 (3)	2632 (3)	104 (3)	81 (2)	81 (3)	−9 (4)	60 (5)	16 (4)
C(56)	8134 (3)	2964 (2)	2243 (3)	96 (3)	73 (2)	80 (3)	−1 (4)	56 (5)	−17 (4)

Table 3. *Atomic parameters of hydrogen atoms in the α form, with their e.s.d.'s in parentheses*

Thermal parameters are in the form $\exp[-B(\sin\theta/\lambda)^2]$. Positional parameters are $\times 10^3$.

	x	y	z	B
H(4A)	836 (3)	441 (2)	28 (3)	5·0 (6)
H(4B)	708 (3)	461 (2)	−88 (2)	4·3 (6)
H(5)	586 (2)	395 (2)	2 (2)	3·3 (5)
H(12)	525 (3)	322 (2)	160 (2)	5·2 (6)
H(13)	396 (3)	304 (2)	267 (3)	6·2 (7)
H(14)	366 (3)	433 (3)	379 (3)	8·5 (8)
H(15)	472 (3)	583 (2)	388 (3)	6·4 (7)
H(16)	602 (3)	600 (2)	273 (2)	5·1 (6)
H(32)	729 (3)	746 (2)	106 (3)	6·4 (7)
H(33)	807 (3)	887 (3)	34 (3)	8·4 (8)
H(34)	918 (3)	871 (2)	−89 (3)	5·7 (7)
H(35)	955 (3)	717 (2)	−150 (3)	5·9 (7)
H(36)	871 (3)	579 (2)	−95 (3)	6·4 (7)
H(52)	655 (3)	242 (2)	−56 (3)	5·2 (6)
H(53)	761 (3)	94 (2)	9 (3)	5·4 (6)
H(55)	926 (3)	199 (2)	346 (3)	5·8 (7)
H(56)	825 (2)	350 (2)	280 (2)	4·6 (6)

Table 5. *Atomic parameters of hydrogen atoms in the β form*

Positional parameters are $\times 10^3$.

	x	y	z	B
H(4A)	270 (3)	124 (9)	276 (3)	3·9 (11)
H(4B)	228 (3)	−28 (9)	337 (3)	4·2 (11)
H(5)	286 (3)	154 (9)	441 (3)	4·4 (12)
H(12)	328 (3)	465 (10)	535 (3)	5·8 (14)
H(13)	341 (3)	743 (10)	644 (4)	6·4 (14)
H(14)	254 (3)	1064 (11)	657 (4)	7·5 (16)
H(15)	160 (3)	1093 (9)	550 (3)	4·6 (12)
H(16)	143 (3)	819 (9)	444 (3)	4·1 (11)
H(32)	58 (2)	565 (8)	254 (3)	2·2 (9)
H(33)	−21 (3)	539 (11)	136 (4)	6·6 (15)
H(34)	−21 (3)	174 (10)	55 (3)	5·8 (14)
H(35)	76 (3)	−116 (11)	80 (4)	6·6 (15)
H(36)	163 (3)	−51 (10)	192 (3)	5·5 (13)
H(52)	418 (3)	136 (9)	452 (3)	4·5 (12)
H(53)	530 (3)	315 (9)	422 (3)	4·6 (12)
H(55)	422 (3)	825 (9)	286 (3)	3·6 (11)
H(56)	309 (3)	655 (8)	308 (3)	3·5 (10)

Table 4. *Atomic parameters of the heavy atoms in the β form* $(\times 10^4; \text{ except } \beta_{22})$

	x	y	z	β_{11}	β_{22} $(\times 10^3)$	β_{33}	β_{12}	β_{13}	β_{23}
Cl	5629·1 (9)	7299 (4)	3396 (2)	36·7 (6)	55·3 (9)	63·1 (9)	−68 (4)	1 (2)	23 (5)
N(1)	2299 (3)	4587 (9)	4125 (3)	27 (2)	43 (3)	34 (2)	56 (10)	−15 (3)	−92 (11)
N(2)	1716 (3)	4733 (9)	3544 (3)	25 (2)	34 (2)	33 (2)	1 (9)	−0 (3)	−29 (10)
C(3)	1760 (3)	3017 (10)	3019 (3)	25 (2)	25 (3)	28 (2)	−9 (10)	5 (3)	−6 (11)
C(4)	2410 (3)	1437 (10)	3208 (3)	31 (2)	24 (2)	34 (3)	18 (11)	4 (4)	3 (12)
C(5)	2826 (3)	2723 (11)	3952 (3)	31 (2)	32 (3)	28 (2)	43 (11)	0 (4)	11 (12)
C(11)	2358 (3)	6200 (10)	4770 (3)	23 (2)	36 (3)	29 (3)	−30 (11)	8 (3)	−40 (12)
C(12)	2933 (3)	6009 (12)	5374 (4)	35 (2)	47 (3)	31 (3)	38 (13)	4 (4)	−57 (14)
C(13)	2999 (3)	7657 (13)	6014 (4)	33 (2)	58 (4)	35 (3)	6 (14)	−0 (4)	−69 (16)
C(14)	2513 (4)	9466 (13)	6075 (4)	38 (3)	53 (4)	39 (3)	−29 (14)	11 (4)	−99 (16)
C(15)	1930 (3)	9644 (12)	5481 (4)	36 (3)	42 (3)	47 (3)	23 (13)	27 (4)	−73 (15)
C(16)	1858 (3)	8036 (10)	4835 (3)	22 (2)	36 (3)	37 (3)	−20 (11)	7 (3)	−44 (13)
C(31)	1213 (3)	2675 (10)	2323 (3)	23 (2)	29 (3)	29 (2)	−20 (11)	8 (3)	−2 (12)
C(32)	659 (3)	4334 (11)	2165 (3)	28 (2)	35 (3)	31 (3)	12 (11)	8 (4)	−40 (13)
C(33)	147 (3)	4019 (13)	1506 (4)	27 (2)	50 (3)	45 (3)	19 (13)	−13 (4)	−33 (16)
C(34)	182 (3)	2008 (13)	1014 (4)	29 (2)	57 (4)	41 (3)	−38 (14)	−13 (4)	−75 (16)
C(35)	726 (3)	337 (12)	1165 (4)	33 (2)	41 (3)	45 (3)	−1 (13)	4 (4)	−90 (15)
C(36)	1238 (3)	671 (11)	1821 (4)	30 (2)	37 (3)	37 (3)	6 (12)	−1 (4)	−57 (14)
C(51)	3528 (3)	3794 (10)	3793 (3)	29 (2)	26 (2)	27 (2)	18 (10)	−2 (3)	−29 (11)
C(52)	4168 (3)	2799 (10)	4134 (4)	29 (2)	30 (3)	36 (3)	40 (11)	−15 (4)	32 (13)
C(53)	4812 (3)	3840 (12)	4006 (4)	24 (2)	43 (3)	44 (3)	32 (12)	−5 (4)	17 (14)
C(54)	4819 (3)	5901 (11)	3539 (4)	32 (2)	36 (3)	35 (3)	−8 (12)	3 (4)	−10 (13)
C(55)	4188 (3)	6903 (11)	3189 (4)	41 (3)	34 (3)	36 (3)	19 (13)	−4 (4)	46 (13)
C(56)	3545 (3)	5863 (11)	3314 (4)	27 (2)	31 (3)	40 (3)	74 (11)	−14 (4)	−3 (13)

Description of the structure and discussion

The molecular structures of both forms projected on the pyrazoline plane are illustrated in Fig. 1, together with the numbering system of atoms in the molecule. The selected bond lengths and bond angles are listed in Table 6. It is most remarkable that the p-chlorophenyl group makes a different angle with the pyrazoline group in the two forms, as is clearly shown in Fig. 1.

The dihedral angles between the phenyl plane and the PYR plane (see below) are 63·5 (4) and 80·1 (3)° for α and β forms respectively. The torsion angles along N(1)—C(5)—C(51)—C(56) are −20·5 and −42·2°. The C(5)—C(51) bond makes an angle of 53·2° with the normal of the PYR plane in the α form, whereas it is 31·0° in the β form. These conformations are considered to be those in which the steric repulsion between H atoms in the p-chlorophenyl group and the diphenyl-
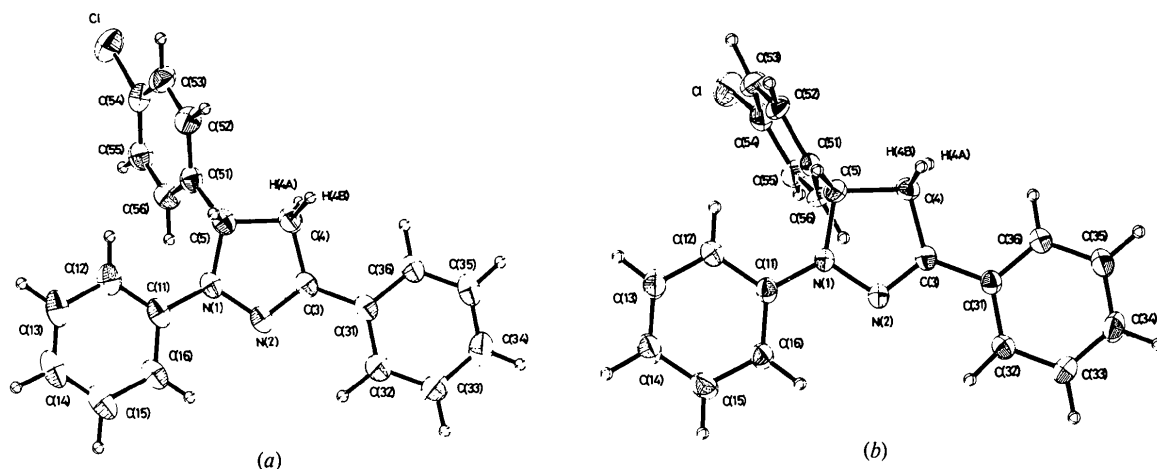
(a)

(b)

Fig. 1. Molecular structures of (a) α and (b) β forms drawn by ORTEP (Johnson, 1965). The thermal ellipsoids are drawn at 30% probability level; hydrogen atoms are shown with an arbitrary temperature factor.

Table 6. Bond lengths (Å) and angles (°), with their e.s.d.'s in parentheses

(i) Bond lengths

	α Form	β Form		α Form	β Form
C(11)—N(1)	1·398 (3)	1·383 (7)	C(15)—C(16)	1·392 (5)	1·382 (8)
N(1)—N(2)	1·389 (3)	1·380 (7)	C(16)—C(11)	1·388 (4)	1·393 (8)
N(2)—C(3)	1·284 (3)	1·292 (7)	C(31)—C(32)	1·390 (4)	1·389 (8)
C(3)—C(31)	1·464 (4)	1·470 (7)	C(32)—C(33)	1·373 (5)	1·385 (9)
C(3)—C(4)	1·500 (4)	1·504 (7)	C(33)—C(34)	1·380 (5)	1·379 (10)
C(4)—C(5)	1·542 (4)	1·555 (8)	C(34)—C(35)	1·364 (5)	1·378 (9)
C(5)—N(1)	1·479 (3)	1·476 (7)	C(35)—C(36)	1·384 (4)	1·383 (8)
C(5)—C(51)	1·507 (4)	1·498 (8)	C(36)—C(31)	1·387 (4)	1·384 (8)
C(4)—H(4A)	0·98 (3)	0·98 (5)	C(51)—C(52)	1·391 (4)	1·385 (8)
C(4)—H(4B)	0·98 (3)	1·02 (5)	C(52)—C(53)	1·373 (4)	1·379 (8)
C(5)—H(5)	0·97 (3)	1·00 (5)	C(53)—C(54)	1·379 (4)	1·373 (9)
C(11)—C(12)	1·395 (4)	1·394 (8)	C(54)—C(55)	1·372 (4)	1·379 (8)
C(12)—C(13)	1·393 (4)	1·388 (9)	C(55)—C(56)	1·376 (4)	1·375 (8)
C(13)—C(14)	1·374 (5)	1·362 (10)	C(56)—C(51)	1·388 (4)	1·389 (8)
C(14)—C(15)	1·372 (5)	1·395 (9)	Cl—C(54)	1·745 (3)	1·747 (6)

(ii) Bond angles

	α Form	β Form		α Form	β Form
C(11)—N(1)—N(2)	117·8 (3)	119·5 (5)	C(3)—C(31)—C(32)	121·4 (3)	120·7 (5)
C(11)—N(1)—C(5)	123·7 (3)	126·6 (5)	C(3)—C(31)—C(36)	120·2 (3)	120·4 (5)
C(5)—N(1)—N(2)	111·9 (3)	113·9 (5)	C(36)—C(31)—C(32)	118·4 (3)	118·9 (6)
N(1)—N(2)—C(3)	108·9 (3)	108·8 (5)	C(31)—C(32)—C(33)	120·6 (4)	120·7 (6)
N(2)—C(3)—C(4)	113·5 (3)	113·1 (5)	C(32)—C(33)—C(34)	120·5 (4)	119·4 (7)
N(2)—C(3)—C(31)	121·9 (3)	122·0 (5)	C(33)—C(34)—C(35)	119·4 (4)	120·6 (7)
C(4)—C(3)—C(31)	124·5 (3)	124·9 (5)	C(34)—C(35)—C(36)	120·8 (4)	119·6 (6)
C(3)—C(4)—C(5)	102·5 (3)	103·3 (5)	C(35)—C(36)—C(31)	120·3 (3)	120·7 (6)
C(4)—C(5)—N(1)	101·1 (3)	100·3 (5)	C(5)—C(51)—C(52)	119·3 (3)	121·2 (5)
C(4)—C(5)—C(51)	112·6 (3)	114·6 (5)	C(5)—C(51)—C(56)	122·7 (3)	120·0 (5)
N(1)—C(5)—C(51)	114·8 (3)	112·8 (5)	C(56)—C(51)—C(52)	117·9 (3)	118·8 (5)
N(1)—C(11)—C(12)	121·0 (3)	119·8 (6)	C(51)—C(52)—C(53)	121·6 (3)	121·0 (6)
N(1)—C(11)—C(16)	120·1 (3)	121·7 (6)	C(52)—C(53)—C(54)	118·8 (3)	119·5 (6)
C(16)—C(11)—C(12)	118·8 (3)	118·5 (6)	C(53)—C(54)—C(55)	121·2 (3)	120·3 (6)
C(11)—C(12)—C(13)	120·0 (3)	119·7 (6)	C(54)—C(55)—C(56)	119·4 (3)	120·3 (6)
C(12)—C(13)—C(14)	120·8 (4)	121·9 (7)	C(55)—C(56)—C(51)	121·2 (3)	120·2 (6)
C(13)—C(14)—C(15)	119·5 (4)	118·8 (7)	Cl—C(54)—C(53)	119·1 (3)	120·2 (5)
C(14)—C(15)—C(16)	120·7 (4)	120·2 (6)	Cl—C(54)—C(55)	119·8 (3)	119·5 (5)
C(15)—C(16)—C(11)	120·3 (3)	120·9 (6)			

pyrazoline moiety are minimized. On the other hand, non-bonded distances between N(1) and H(56) are 2·55 (3) and 2·63 (5) Å in α and β forms, respectively, which are somewhat shorter than the sum of the van der Waals radii of 2·7 Å (Pauling, 1960). This compound forms a stable glassy state, as mentioned above, whereas DPP does not form any glassy state (Sano, Kato, Yokoyama, Shirota & Mikawa, 1976). These facts and the observed dimorphism of the present compound strongly suggest that the relatively free change in the conformation of the p-chlorophenyl group has a close relation to the glass-forming ability of Cl-PDPP.

It is important to investigate the degree of conjugation in the diphenylpyrazoline moiety, because it may influence the optical and photoconductive properties. The bond lengths in the pyrazoline moieties of
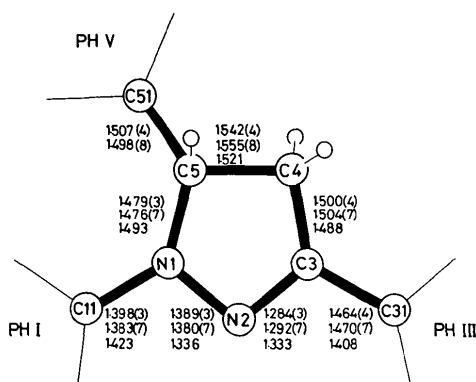

Fig. 2. Bond lengths (Å) in the pyrazoline moiety, with their e.s.d.'s in parentheses. The upper values are for the α form, middle for the β form and lower for DPP. The average e.s.d. for DPP is 0·007 Å.

both forms are illustrated in Fig. 2 together with those of DPP. It is easy to recognize that significant differences are not observed in these bond lengths in the α and β forms of Cl-PDPP. However, some important differences exist between DPP and Cl-PDPP. The C(11)—N(1) and N(2)—C(3) lengths are shorter in Cl-PDPP than in DPP, which means the increase of double-bond character in these bonds. On the other hand, the N(1)—N(2) and C(3)—C(31) bonds are longer and have increasing single-bond character. This means that π electrons are less conjugated in Cl-PDPP than in DPP. It may be concluded that the introduction of a p-chlorophenyl substituent on DPP causes this change in the conjugation of the diphenylpyrazoline moiety. These bond lengths, of course, are still correspondingly longer or shorter than the generally accepted values for pure double and single bonds (Wheatley, 1955; Herbstein & Schmidt, 1955; Donohue, Lavine & Rollet, 1956; Sabesan & Venkatesan, 1971). For example, the N(2)—C(3) bond length is significantly longer than the value of 1·255 Å in pyrazoline hydrochloride in which the C—N bond appears to be a pure double bond (Nardelli & Fava, 1962). Therefore, the delocalization of π electrons must exist to some extent in the diphenylpyrazoline moiety in Cl-PDPP.

The equations of some least-squares planes, deviations of atoms from the planes, and dihedral angles between these planes are summarized in Table 7. From the χ^2 test for the least-squares plane, it is shown that the pyrazoline ring is highly significantly non-planar with $\chi^2 = 3253·3 (298·1)^*$ (Stout & Jensen, 1968). However, the plane defined by N(1), N(2), C(3)

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* This value is for the α form, with that of the β form in parentheses. Similar expressions are also used in the following text.
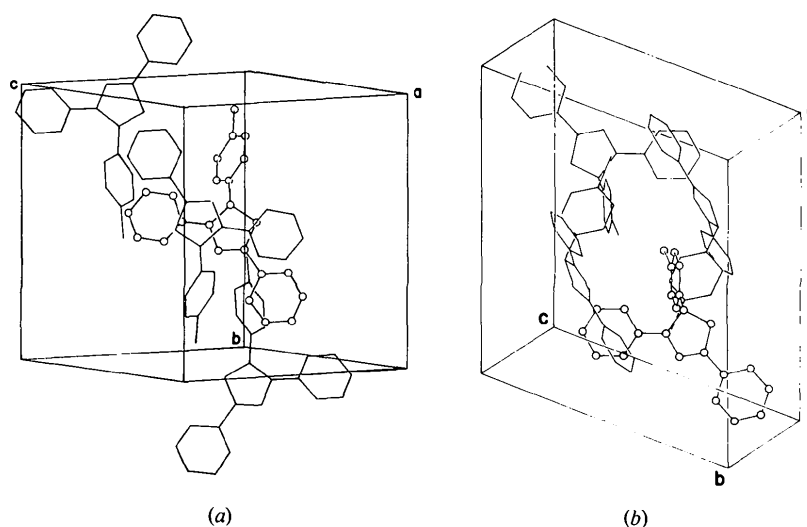

              (a)   (b)

Fig. 3. Crystal structures of (a) α and (b) β forms, viewed along the normal to the PYR plane.

and C(4) atoms gives $\chi^2 = 11\cdot0\,(1\cdot4)$, and the largest deviation of the atoms from the least-squares planes is only 0·005 Å. Therefore, this plane is used as the pyrazoline ring plane and referred to as the PYR plane hereafter (see also Table 7 for the notations of other planes).

Owing to the conjugation between two phenyl rings *via* the N(1), N(2) and C(3) atoms, the diphenyl-pyrazoline moiety would be expected to lie on a plane.

However, the dihedral angles between the PYR plane and the two phenyl rings [PH(I) and PH(III)] show that this moiety is clearly non-planar. The deviations of the atoms from the PYR plane demonstrate this non-planarity. In both forms PH(I) is bent upwards, besides rotating about the C(11)—N(1) bond. Similarly, PH(III) is somewhat bent and rotates about the C(3)—C(31) bond. Moreover, in the α form, the C(5) atom deviates in the same direction for PH(I), indicating that the N(1)

Table 7. *Least-squares planes*

(i) Coefficients of the planes $AX + BY + CZ + D = 0$, where X, Y, Z and D are in Å relative to orthogonal axes **a**, **b** and **c***

		A	B	C	D
Pyrazoline	α	−0·69 (4)	0·22 (5)	−0·69 (4)	4·4 (3)
ring	β	−0·54 (3)	−0·61 (3)	0·58 (4)	−0·4 (2)
PYR	α	−0·702 (4)	0·151 (6)	−0·696 (4)	5·00 (3)
	β	−0·580 (4)	−0·604 (3)	0·546 (4)	−0·11 (6)
PH(I)	α	−0·502 (1)	0·314 (1)	−0·806 (1)	2·704 (1)
	β	−0·593 (3)	−0·612 (3)	0·523 (3)	0·09 (7)
PH(III)	α	−0·601 (3)	0·053 (4)	−0·797 (2)	5·05 (2)
	β	−0·627 (2)	−0·520 (2)	0·580 (2)	−0·295 (8)
PH(V)	α	−0·923 (2)	−0·315 (4)	0·221 (4)	8·330 (9)
	β	−0·129 (3)	0·571 (2)	0·811 (2)	−5·484 (3)

(ii) Atomic deviations (Å) from the planes. Atoms used to define the planes are marked with asterisks.

	Pyrazoline ring		PYR		PH(I)		PH(III)		PH(V)	
	α	β	α	β	α	β	α	β	α	β
N(1)	−0·068*	0·056*	−0·003*	−0·001*	−0·034	−0·020	−0·071	0·097	0·274	1·002
N(2)	0·028*	−0·017*	0·005*	0·003*	0·303	0·019	−0·120	0·121	−0·619	0·400
C(3)	0·017*	−0·043*	−0·005*	−0·004*	0·568	0·036	0·056	−0·003	−1·645	−0·863
C(4)	−0·070*	0·031*	0·003*	0·002*	0·459	0·027	0·278	−0·115	−1·555	−1·259
C(5)	0·097*	−0·035*	0·230	−0·132	0·255	−0·149	0·407	−0·177	−0·106	0·055
C(11)			0·371	0·047	0·000*	−0·003*				
C(12)			0·705	0·090	0·000*	0·006*				
C(13)			1·043	0·114	0·001*	−0·002*				
C(14)			1·049	0·105	−0·001*	−0·008*				
C(15)			0·724	0·086	0·001*	0·006*				
C(16)			0·383	0·050	0·000*	0·002*				
C(31)			−0·051	0·008			0·007*	−0·004*		
C(32)			0·138	−0·096			−0·009*	0·006*		
C(33)			0·149	−0·094			0·004*	−0·005*		
C(34)			−0·058	0·040			0·002*	0·002*		
C(35)			−0·266	0·152			−0·004*	−0·001*		
C(36)			−0·265	0·142			−0·001*	0·002*		
C(51)			−0·674	−1·415					−0·006*	0·004*
C(52)			−0·328	−1·442					0·006*	−0·001*
C(53)			−1·161	−2·620					0·001*	−0·004*
C(54)			−2·364	−3·782					−0·008*	0·006*
C(55)			−2·726	−3·777					0·007*	−0·002*
C(56)			−1·887	−2·603					−0·001*	−0·003*
Cl			−3·448	−5·275					−0·064	0·053

(iii) Dihedral angles (°) between the planes

		PH(I)	PH(III)	PH(V)
PYR	α	16·1 (3)	9·9 (4)	63·5 (4)
	β	1·6 (3)	5·8 (3)	80·1 (3)
PH(I)	α		16·1 (2)	79·3 (2)
	β		6·5 (3)	81·3 (3)
PH(III)	α			68·8 (3)
	β			75·3 (2)

atom has a significant deviation from a sp^2 planar hybridization. In the β form, however, the C(5) atom deviates in the opposite direction. The deviation of the N(1) atom from the plane defined by the C(11), N(2) and C(5) atoms is 0·214 (0·023) Å. Therefore, the nonplanarity of the diphenylpyrazoline moiety is more manifest in the α form. The reason is not obvious at present, but the intra- and intermolecular interactions which cause the different conformations of the three phenyl groups in the two forms must be related to this observation.

The molecular packing in the unit cell viewed along the normal to the PYR plane is shown in Fig. 3. The intermolecular distances, which are close to the sum of van der Waals radii in the α form, are as follows: Cl···H(36) at $(x, \frac{1}{2}-y, \frac{1}{2}+z)$ 2·88 (3) Å, H(55)···C(36) at $(2-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ 2·89 (3) Å, C(15)···H(4B) at $(1-x, 1-y, -z)$ 2·96 (3) Å. These contacts may account for the rotation of each phenyl group. Similarly, the short contacts found in the β form are: Cl···H(12) at $(1-x, 1-y, 1-z)$ 2·95 (6) Å, C(16)···H(4B) at $(x, 1+y, z)$ 2·80 (5) Å, C(33)···H(32) at $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ 2·87 (4) Å.

The overlapping of π-electron clouds between neighbouring molecules must have a close relation to the photoconductivity. However, no pair of neighbouring molecules is found, in which the π-electron clouds of pyrazoline overlap.

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3-Ammonio-1,6-anhydro-3-deoxy-β-D-glucopyranose Chloride Monohydrate

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$C_6H_{14}NO_5Cl$, $M_r = 215·6$; orthorhombic, $P2_12_12_1$, $a = 6·2915$ (5), $b = 6·8874$ (8), $c = 21·8987$ (15) Å; $V = 947·6$ Å^3; $Z = 4$; $D_m = 1·510$ g cm^{-3}, $D_x = 1·511$ g cm^{-3}, $R = 0·029$ and $R_w = 0·039$ for 1163 reflections. The $B_{0,3}$ boat conformation deduced from ^1H NMR data is not observed. Instead the pyranose ring is a distorted $^1C_4$ chair. The anhydro ring has a $^0T_5$ twist conformation. The hydrogen bonding involves all available (N$^+$)H and (O)H atoms, the water molecules and the chloride ions, but not the ring oxygens.

Introduction

This work is an extension of the study of the conformation and structural properties of 1,6-anhydro-β-D-

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glucopyranose and its 3-amino deoxy derivative (Park, Kim & Jeffrey, 1971; Noordik & Jeffrey, 1977). The crystals were provided by Professor M. Cerny, Charles University, Praha, Czechoslovakia, who reported that the 3-amino hydrochloride in solution gave NMR data indicating that the pyranose ring had the $B_{0,3}$ boat conformation (Trnka, Cerny, Budesinsky & Pacek, 1975).

A crystal of dimensions 0·27 × 0·27 × 0·12 mm