Table 4. *Dihedral angles* (°) *for the three rings*

1-2-3-4	-41	6-11-12-O	-33
2-3-4-5	63	11-12-O-7	33
3-4-5-10	-48	12-O-7-6	-18
4-5-10-1	18	O-7-6-11	3
5-10-1-2	-3	7-6-11-12	21
5-6-7-8	-12		
6-7-8-9	-40		
7-8-9-10	52		
8-9-10-5	-12		
9-10-5-6	-39		

the cyclohexane ring has a conformation between the boat and twisted-boat forms (Hendrickson, 1967). Both rings have only C_2 symmetry. The five-membered ring has the envelope conformation with atom C(12) lying 'below' the plane through atoms C(11), C(6), C(7) and O(1) depicted in Fig. 3. A conformation with C(12) 'above' the plane can be approximately generated (authors' program, unpublished) by a rotation of C(12) around the C(6)–C(11) axis until at 38·5° the C(12)–O(1) distance becomes the same. The HC(11)–HC(4) distance however is then decreased from 2·00 to 1·77 Å, based on calculated H positions. There are two inter-molecular hydrogen bonds, O(2)–H···O(3)' $(1-y,$ $x-1, z-\frac{1}{4})$ and O(3)–H···O(2)' $(1+x,y,z)$, 2·764 (9) and 2·766 (9) Å respectively. The torsion angles H–O–C–O' are each 2°; this indicates that the H atoms are practically as close as possible to the O' atoms, in keeping with the partially electrostatic nature of the hydrogen bond. The attraction H···O' is partly balanced by the deviations, indicated by the torsion angles H–O(2)–C(4)–C(5) (65°) and H–O(3)–C(9)–C(8) (45°), of the H atoms from the staggered positions.

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p-Phenylenedi[α-cyanoacrylic Acid] Di-n-propyl Ester, a Photopolymerizable Crystal

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Abstract. $C_{20}H_{20}N_2O_4$, M.W. 352·4. Monoclinic, $P2_1/n$(No. 14), $a=5\cdot341$ (2), $b=26\cdot112$ (7), $c=6\cdot882$ (2) Å, $\beta=103\cdot81$ (2)°. $Z=2$, $D_x=1\cdot265$, $D_m=1\cdot262$ g cm^{-3}. The molecules are nearly planar and are piled up, with displacement in the direction of the long molecular axis, to form a parallel plane-to-plane stack along the c axis. In the stack double bonds related by the centre of symmetry are situated at the shortest distance of 3·931 Å.

Introduction. A group of diolefinic compounds are photopolymerized in the crystalline state to give a three-dimensionally oriented polymer containing a cyclobutane ring in the main chain (for a review see Hasegawa, Suzuki, Nakanishi & Nakanishi, 1973). In order to clarify the polymerization mechanism, we have been studying the crystal structures of the diolefins and have discussed the mechanism on the basis of crystal structures of monomers and polymers (Naka-nishi, Hasegawa & Sasada, 1972). The present compound, p-phenylenedi[α-cyanoacrylic acid] di-n-propyl ester (p-CPAnPr), is a tri-substituted olefin and shows the highest rate of polymerization among the group of compounds at room temperature.

p-CPAnPr was synthesized by the method of Nakanishi & Hasegawa (1969). Colourless plate-like crystals were grown from a tetrahydrofuran solution by slow evaporation. The space group was determined from Weissenberg photographs. The precise lattice constants and intensity data were derived from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. The specimen used was a fragment of a plate, 0·20 × 0·25 × 0·10 mm. All reflexions within the range of $2\theta < 56°$ were collected by use of the 2θ–ω scan mode with a scanning rate of 2° min^{-1}. Stationary background counts were accumulated for 10 s before and after each scan. Out of 2295 reflexions, 1669

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^3$)

The form of the anisotropic thermal parameters is 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}
C(1)	11834 (6)	251 (1)	−739 (4)	37 (1)	1·52 (5)	25·3 (8)	−2·6 (4)	35 (2)	−1·6 (3)
C(2)	11015 (6)	464 (1)	841 (4)	38 (1)	1·47 (5)	25·9 (8)	−2·7 (4)	35 (2)	−2·5 (3)
C(3)	9129 (5)	214 (1)	1604 (4)	31 (1)	1·34 (4)	20·1 (6)	0·1 (3)	24 (1)	−0·5 (3)
C(4)	8072 (5)	405 (1)	3256 (4)	33 (1)	1·44 (5)	21·5 (7)	−0·8 (4)	27 (1)	−0·5 (3)
C(5)	8452 (5)	847 (1)	4288 (4)	33 (1)	1·39 (4)	19·5 (6)	−0·2 (4)	24 (1)	−0·4 (3)
C(6)	7028 (6)	934 (1)	5889 (4)	43 (1)	1·46 (5)	21·1 (7)	0·4 (4)	30 (2)	−1·1 (3)
O(1)	5531 (5)	629 (1)	6279 (4)	60 (1)	1·67 (4)	36·9 (7)	−4·4 (3)	65 (2)	−2·8 (3)
O(2)	7600 (4)	1378 (1)	6796 (3)	52 (1)	1·66 (4)	26·7 (6)	−3·1 (3)	44 (1)	−3·3 (3)
C(7)	6204 (7)	1503 (1)	8339 (5)	67 (2)	1·79 (6)	26·8 (9)	−1·5 (5)	54 (2)	−3·2 (4)
C(8)	6652 (8)	2041 (1)	8898 (6)	69 (2)	1·83 (6)	41·1 (12)	−1·7 (6)	69 (3)	−3·5 (4)
C(9)	5196 (8)	2196 (1)	10466 (6)	75 (2)	2·11 (7)	39·1 (12)	0·5 (6)	65 (3)	−4·2 (5)
C(10)	10149 (6)	1247 (1)	3960 (4)	43 (1)	1·50 (5)	23·0 (7)	0·1 (4)	30 (2)	−1·3 (3)
N(1)	11476 (6)	1565 (1)	3677 (5)	67 (2)	1·86 (5)	41·4 (10)	−6·5 (5)	61 (2)	−2·9 (4)

Table 1 (cont.)

	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^3$)	B (Å^2)	C–H (Å)
H(C1)	1314 (7)	43 (1)	−135 (5)	4·2 (9)	1·01 (3)
H(C2)	1173 (6)	80 (1)	149 (5)	3·9 (8)	1·03 (3)
H(C4)	689 (7)	16 (1)	373 (5)	4·4 (9)	1·01 (3)
H(C7)1	684 (7)	128 (1)	961 (5)	4·6 (9)	1·04 (4)
H(C7)2	413 (8)	146 (2)	767 (6)	6·7 (11)	1·10 (4)
H(C8)1	610 (8)	225 (2)	758 (6)	6·1 (11)	1·03 (4)
H(C8)2	865 (8)	208 (2)	958 (7)	7·5 (11)	1·06 (4)
H(C9)1	544 (9)	256 (2)	1082 (7)	8·2 (13)	0·99 (4)
H(C9)2	574 (7)	199 (1)	1176 (6)	5·5 (10)	1·02 (4)
H(C9)3	327 (8)	212 (2)	981 (7)	7·7 (12)	1·04 (4)

were greater than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption ($\mu = 1·06$ cm^{-1}).

The space group and Z indicated that the molecule must have a centre of symmetry. By iterative symbolic addition procedures, the signs of 261 reflexions out of 297 with $|E| \geq 1·4$ were determined in terms of two symbols. One of four E maps revealed the positions of all non-hydrogen atoms. The parameters were refined by the block-diagonal least-squares method using $w = 0·5$ for $|F_o| \leq 1·0$, $1·0$ for $|F_o| > 1·0$. Isotropic hydrogen atoms were first located geometrically and then refined. In the final refinement, the five strongest reflexions were excluded because they seemed to suffer from secondary extinction. The final R value was

0·068 for 1664 reflexions.* 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 related compounds, except for the C(2)–C(3)–C(4), C(3)–C(4)–C(5), C(4)–C(5)–C(10) angles; they are considerably larger than the sp^2 angle. The benzene ring, and carbonyl and cyanoethylene [C(3)–C(4)–C(5)–C(6)··· C(10)–N(1)] groups are planar.* The benzene ring rotates by 5·2° about the bond C(3)–C(4) from the cyanoethylenic plane, and the carbonyl rotates by only 0·9° about C(5)–C(6) in the same direction. Thus, the molecular skeleton consisting of the above three groups is nearly planar, within the deviation of 0·09 Å from the mean plane.* The n-propyl group rotates by 11·4° about O(2)–C(7).

* 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 31663 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
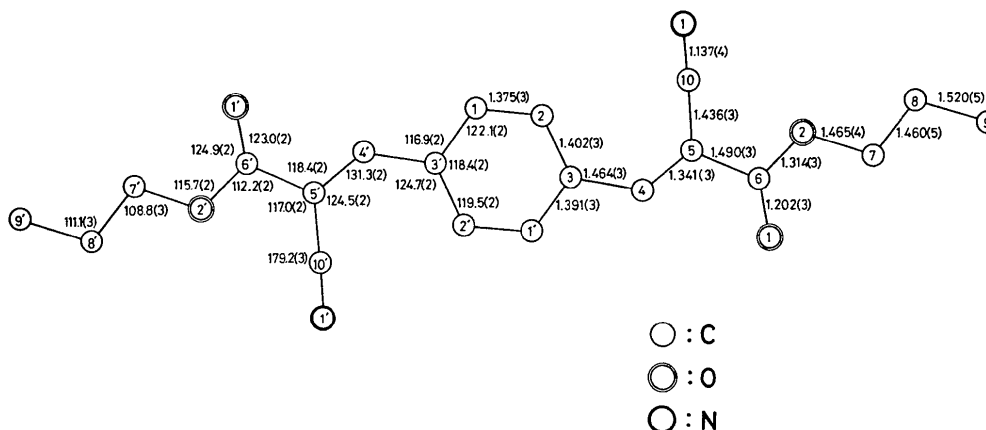

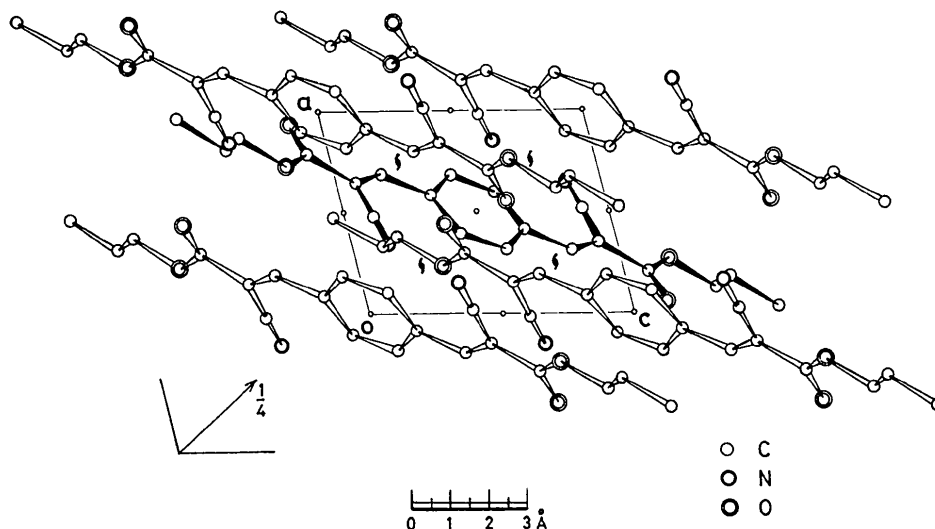Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

Fig. 2. The crystal structure viewed along the b axis.

O C
O N
O O

The crystal structure viewed along the b axis is shown in Fig. 2. The molecules are piled up along the c axis and displaced in the direction of the long molecular axis by about half a molecule, to form a parallel plane-to-plane stack. In the stack, double bonds related by the centre of symmetry approach at the shortest distance of 3·931 Å (Table 2), which is very close to the 3·939 Å found in 2,5-distyrylpyrazine (DSP) (Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971). The second shortest distance of 5·331 Å is found between the molecules in different stacks ([10$\bar{1}$] translation) and is too great for reaction to occur (Hirshfeld & Schmidt, 1964). Therefore, it is most probable that the double bonds in the stack react to form a cyclobutane ring, and consequently polymer chains should grow in the direction of the c axis. Fig. 3 shows the intermolecular contacts of reactive molecules. The electron-rich carbonyl group approaches the electron-deficient benzene ring. A similar type of intermolecular contact has also been observed in DSP, and may be a predominant motif for the formation of a photopolymerizable crystal of this kind.

O C
O N
O O

Fig. 3. The overlapping of reactive molecules viewed along the normal of the mean plane of the molecule.

Table 2. *Intermolecular distances between double bonds* (Å)

C(4^i)···C(4$^{'ii}$)	5·293	C(4^i)···C(5$^{'iv}$)	3·931
C(4^i)···C(5$^{'ii}$)	6·383	C(5^i)···C(5$^{'iv}$)	4·740
C(5^i)···C(5$^{'ii}$)	7·555	C(4^i)···C(4$^{'v}$)	11·263
C(4^i)···C(4$^{'iii}$)	4·963	C(4^i)···C(5$^{'v}$)	10·159
C(4^i)···C(5$^{'iii}$)	5·331	C(5^i)···C(4$^{'v}$)	10·178
C(5^i)···C(5$^{'iii}$)	5·984	C(5^i)···C(5$^{'v}$)	9·037
C(4^i)···C(4$^{'iv}$)	3·469		

Symmetry code

[Reference molecule i is around the centre of symmetry (1,0,0).]

Superscript

i	x	y	z	iv	x	y	$1+z$
ii	$-1+x$	y	z	v	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	$-1+x$	y	$1+z$				

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