

***p*-Phenylenediacrylic Acid Diphenyl Ester (*p*-PDAPh), a Photopolymerizable Crystal**

BY HACHIRO NAKANISHI AND KATSUHIKO UENO

Research Institute for Polymers and Textiles, Sawatari, Kanagawa-ku, Yokohama 221, Japan

AND YOSHIO SASADA

Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

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Abstract. C₂₄H₁₈O₄, *M_r* = 370.4, monoclinic, *P*2₁/*c*, *a* = 6.935 (1), *b* = 18.611 (6), *c* = 7.570 (2) Å, β = 101.88 (2)°, *Z* = 2, *D_x* = 1.287, *D_m* = 1.285 g cm⁻³. Despite comparatively poor molecular planarity, the molecules form the plane-to-plane stack which is a common feature of the packing of photopolymerizable crystals of this kind. In the stack, double bonds related by a centre of symmetry have a closest approach of 3.928 Å.

Introduction. *p*-PDAPh was synthesized according to Suzuki, Suzuki, Nakanishi & Hasegawa (1969). Colourless plate-like crystals were grown from a benzene solution by slow evaporation. The specimen used was a fragment of a plate 0.10 × 0.05 × 0.03 mm. The space group was determined from photographs. The precise lattice constants and intensity data were obtained from measurements on a Rigaku computer-controlled four-circle diffractometer, with graphite-monochromatized Mo *K*α radiation. All reflexions within the range 2θ < 60° were collected with the 2θ-ω scan mode and a scanning rate of 4° min⁻¹. Stationary background counts were accumulated for 10 s before and after each scan. Of 2787 reflexions, only 658 were greater than 3σ(|*F_o*|) and used for structure determination. No correction was made for absorption (μ = 1.03 cm⁻¹).

By iterative symbolic addition procedures, the signs of 226 reflexions (of the 342 with |*E*| ≥ 1.5) were determined in terms of three symbols. One of the eight *E* maps revealed the positions of all the non-hydrogen atoms. The parameters were refined by the block-diagonal least-squares method using *w* = 0.5 for |*F_o*| < 1.0, 1.0 for |*F_o*| ≥ 1.0. Isotropic H atoms were first located geometrically and then refined. The final *R* value was 0.057.* Atomic scattering factors were taken

Table 1. Fractional atomic coordinates (× 10⁴ for C, O; × 10³ for H)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	-1669 (9)	340 (3)	-937 (9)
C(2)	89 (10)	714 (3)	-441 (9)
C(3)	1781 (9)	390 (3)	528 (8)
C(4)	3590 (9)	814 (3)	1074 (8)
C(5)	5155 (9)	627 (3)	2311 (9)
C(6)	6798 (9)	1135 (3)	2812 (9)
O(1)	8046 (6)	885 (2)	4327 (6)
O(2)	7028 (7)	1681 (2)	2089 (7)
C(7)	9695 (9)	1314 (3)	5069 (8)
C(8)	9436 (9)	1972 (3)	5843 (8)
C(9)	11504 (9)	1014 (3)	5112 (9)
C(10)	11103 (11)	2337 (3)	6679 (9)
C(11)	13157 (9)	1408 (4)	5946 (9)
C(12)	12964 (10)	2067 (4)	6737 (9)
H(C1)	-290 (9)	64 (3)	-161 (8)
H(C2)	14 (10)	125 (4)	-78 (9)
H(C4)	362 (10)	134 (4)	44 (9)
H(C5)	521 (10)	14 (4)	293 (9)
H(C8)	796 (9)	217 (3)	581 (9)
H(C9)	1165 (10)	50 (4)	456 (9)
H(C10)	1093 (9)	283 (3)	726 (9)
H(C11)	1441 (9)	120 (3)	597 (9)
H(C12)	1421 (9)	234 (3)	742 (9)

Estimated standard deviations are in parentheses.

from *International Tables for X-ray Crystallography* (1962). Final atomic coordinates 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 comparable with those of related compounds (Nakanishi, Ueno & Sasada, 1978). The benzene rings, and ethylene and carbonyl groups are planar.* The central benzene ring rotates 15.9° about C(3)–C(4) from the ethylenic plane, and the carbonyl rotates 10.8° about C(5)–C(6) in the opposite direction; the benzene ring makes a dihedral angle of 24.6° with the

* Lists of structure factors, thermal parameters and deviations of atoms from some least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33377 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See previous footnote.

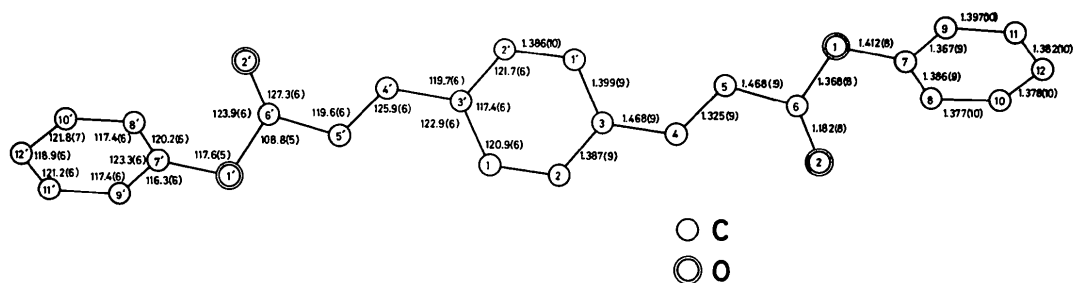


Fig. 1. Bond lengths (Å) and angles (°). The estimated standard deviations are in parentheses.

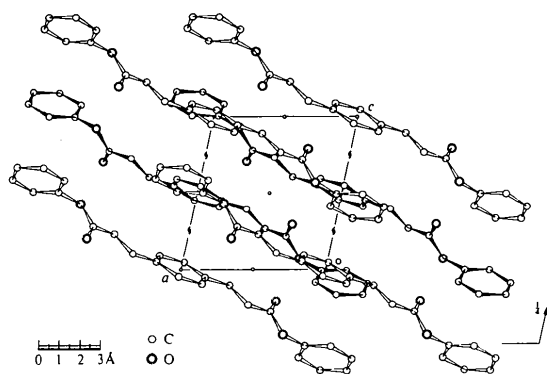


Fig. 2. The crystal structure viewed along the *b* axis.

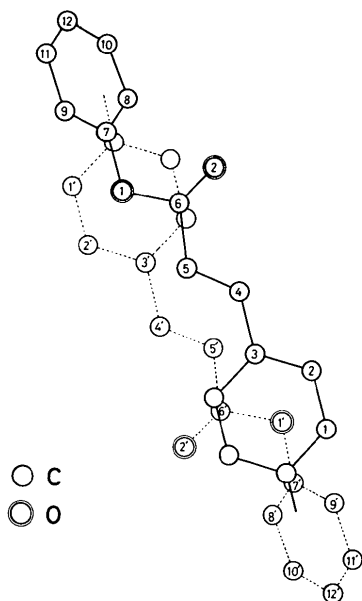


Fig. 3. The overlapping of reacting molecules viewed along the normal of the mean plane of the molecule.

carbonyl group. Thus, the planarity of the molecular skeleton consisting of the above three groups is poor, contrary to the nearly planar conformations of dialkyl

Table 2. Intermolecular distances (Å) between double bonds

C(4 ⁱ)...C(4 ⁱⁱ)	4.117	C(5 ⁱ)...C(5 ⁱⁱⁱ)	4.736
C(4 ⁱ)...C(5 ⁱⁱ)	3.928	C(4 ⁱ)...C(4 ^{iv})	7.330
C(5 ⁱ)...C(5 ⁱⁱ)	4.174	C(4 ⁱ)...C(5 ^{iv})	8.077
C(4 ⁱ)...C(4 ⁱⁱⁱ)	6.598	C(5 ⁱ)...C(4 ^{iv})	7.379
C(4 ⁱ)...C(5 ⁱⁱⁱ)	5.588	C(5 ⁱ)...C(5 ^{iv})	7.933

Symmetry code

(i)	<i>x</i> , <i>y</i> , <i>z</i>	(iii)	1 + <i>x</i> , <i>y</i> , 1 + <i>z</i>
(ii)	1 + <i>x</i> , <i>y</i> , <i>z</i>	(iv)	<i>x</i> , ½ - <i>y</i> , ½ + <i>z</i>

esters of the same acid (Ueno, Nakanishi, Hasegawa & Sasada, 1978; Nakanishi, Ueno & Sasada, 1978). The phenolic benzene ring rotates 65.0° about O(1)—C(7) to bring C(8) closer to O(2) than C(9).

The crystal structure viewed along the *b* axis is shown in Fig. 2. The molecules are piled up along the *c* axis, displaced in the direction of the molecular long axis by about half a molecule, to form a parallel plane-to-plane stack which is a common feature of the packing of the photopolymerizable crystals studied so far. In the stack, double bonds related by a centre of symmetry approach at the shortest distance of 3.928 Å; these would react to form a cyclobutane ring upon photoirradiation because the second shortest distance is >5 Å (Table 2). The resulting polymer chain growth along the stack has been confirmed by the investigation of crystal change during polymerization (Nakanishi, Hasegawa & Sasada, 1977). Fig. 3 shows the intermolecular contacts of reacting molecules. The ester O atom with lone-pair electrons approaches the electron-deficient benzene ring. Such intermolecular contacts will be discussed elsewhere in relation to the crystal-forming motif (Nakanishi, Ueno & Sasada, 1978).

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References

- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201–207. Birmingham: Kynoch Press.
- NAKANISHI, H., HASEGAWA, M. & SASADA, Y. (1977). *J. Polym. Sci. Polym. Phys. Ed.* **15**, 173–191.
- NAKANISHI, H., UENO, K. & SASADA, Y. (1978). *Acta Cryst.* **B34**. In the press.
- SUZUKI, F., SUZUKI, Y., NAKANISHI, H. & HASEGAWA, M. (1969). *J. Polym. Sci. Part A1*, **7**, 2319–2331.
- UENO, K., NAKANISHI, H., HASEGAWA, M. & SASADA, Y. (1978). *B34*, 2034–2035.

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2-Formyl-5-benzylpyridine Thiosemicarbazone

BY JOE N. BROWN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, USA

AND KRISHNA C. AGRAWAL

Department of Pharmacology, School of Medicine, Tulane University, New Orleans, LA 70112, USA

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Abstract. $C_{14}H_{14}N_4S$, monoclinic, $C2/c$, $a = 27.596$ (3), $b = 6.056$ (1), $c = 17.625$ (3) Å, $\beta = 110.51$ (2)°, $M_r = 270.36$, $Z = 8$, $D_c = 1.302$, $D_x = 1.31$ g cm⁻³ (by flotation). The molecular conformation is such that both the pyridine N atom and the S atom are *trans* to N(4). The thiosemicarbazone side chain is planar and twisted 6° relative to the pyridine ring.

Introduction. Crystals of the title compound were grown by slowly cooling a sealed ampoule containing a saturated solution in acetonitrile. The ampoule was placed in a Dewar flask initially containing boiling water and cooled to room temperature over a period of approximately four days. A pale yellow, irregularly shaped crystal approximately 0.33 × 0.17 × 0.10 mm was mounted with the [110] axis coincident with the ϕ axis of a Picker FACS-I computer-controlled diffractometer. Lattice constants were determined by carefully measuring with a narrow slit both plus and minus 2θ values of the Cu $K\alpha_1$, $K\alpha_2$ doublet for 15 reflections with $2\theta > 61^\circ$, curve-fitting the resultant profiles for each reflection, and finally by a least-squares refinement. Three-dimensional intensity data were collected with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) using a variable scan width ($2.4^\circ + 0.72^\circ \tan \theta$), a $\theta/2\theta$ scan (2° min^{-1}), and 10 s background measurements at both extremities of the scan. 2181 independent reflections were measured to a maximum 2θ of 125° ($d = 0.87$ Å). Intensities of three standard reflections, monitored every block of 50 reflections, remained within 5% of their mean values throughout the entire data collection,

indicating both crystal and electronic stability. Structure amplitudes and their estimated errors were calculated from the expressions $|F_o| = (QI_n)^{1/2}$ and $\sigma^2(F_o) = (Q/4I_n) [I_s + (t_s/t_b)^2 I_b + (0.02I_n)^2]$, where Q contains corrections for Lorentz-polarization and absorption, I_s and I_b are the scan and background intensities, t_s and t_b are the scan and background times, and I_n is the net integrated intensity. Absorption was corrected for as a function of ϕ (obtained from a ϕ scan at $\chi = 90^\circ$) with a maximum deviation of 38% (linear $\mu = 19.5$ cm⁻¹ for Cu $K\alpha$ radiation). 1602 (73%) reflections had $|F_o| > 3\sigma(F_o)$ and were used in the structure determination and refinement.

Normalized structure amplitudes, $|E|$'s were calculated from a $K(s)$ curve and rescaled by parity groups (we were unable to solve the structure from $|E|$'s that were normalized, $\langle E^2 \rangle = 1.0$, as a whole rather than by parity groups). The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least squares [minimizing $\sum w(\Delta F)^2$]. The scattering factors for all non-hydrogen atoms were taken from the tabulation of Cromer & Waber (1965) while that for H was from Stewart, Davidson & Simpson (1965). After 15 cycles of isotropic refinement of non-hydrogen atoms, the H atom coordinates were determined from a ΔF map (typical peak heights were 0.5 to 0.7 e Å⁻³). Refinement was terminated after an additional 10 cycles of refinement in which the non-hydrogen atoms were refined with anisotropic temperature factors and the H atoms with isotropic temperature factors. The largest shift was less than 0.1 times its estimated standard