Discussion. Atomic parameters are given in Table 1.* Bond lengths (Table 2) and angles reveal no unusual features.

The benzo (ring 1) and phenyl groups (rings 2 and 3) are close to planar with mean C—C = 1·39 Å. Rings (1) and (2) in *peri* interaction adopt an orthogonal conformation [dihedral angle: 85·7 (3)°], the C(7)–ring (2) bond being purely equatorial [1·2 (3)°, relative to mean plane 1 (see Table 2)]. The N atom displays three different N—C bonds, the shortest N—C(17) [1·392 (7) Å] joining the *N*-phenyl group to the heptaatomic ring (Fig. 1); this large ring has an envelope conformation, the point of it being the N atom (1·07 Å from the mean plane 1); C(8) and C(3) lie closer to the plane (0·76 and 0·60 Å). The ethylene adduct [C(23)=C(24): 1·317 (8) Å] lies in axial configuration with respect to the benzo ring (1) (Fig. 1) and on the other side of this plane. The relative disposition of H(7) and N is thus inverted with respect to the original aziridine (I). The structure clearly corresponds to the diastereoisomer (II′).

This structure determination indicates that the acetylene approaches the aziridine ring (I) from the side in which the H atom is directed and that after the triangular ring opens, the N atom is displaced to the opposite side of the ring.

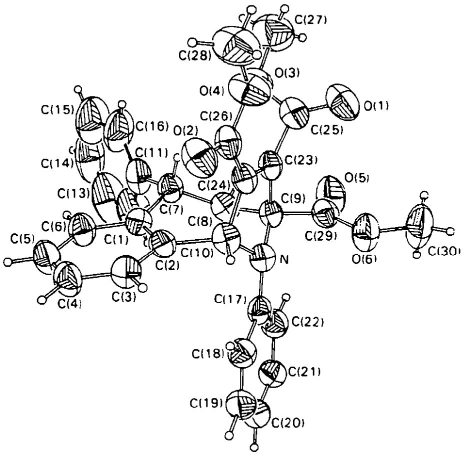

Fig. 1. Thermal-ellipsoid plot (50% probability) of pyrroline molecule (II′), showing the atom-numbering scheme.

References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**(5), 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.
Tinant, B., Declercq, J.-P., Germain, G. & Van Meerssche, M. (1982). *Cryst. Struct. Commun.* **11**(4), 1411–1416.
Vebrel, J., Cerutti, E. & Carrie, R. (1979). *C. R. Acad. Sci. Sér. C*, **288**, 351–354.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39503 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Cinnamoyl Peroxide, $C_{18}H_{14}O_4$

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Abstract. $M_r = 294{\cdot}13$, monoclinic, $P2_1$, $a = 14{\cdot}64$ (2), $b = 9{\cdot}10$ (2), $c = 5{\cdot}63$ (1) Å, $\beta = 93{\cdot}0$ (2)°, $U = 749{\cdot}00$ Å^3, $Z = 2$, $D_x = 1{\cdot}305$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}760$ mm^{-1}, $F(000) = 308$, $T =$ *ca* 293 K. Final $R = 0{\cdot}069$ for 604 unique reflexions. In the crystal the molecule takes up an extended conformation, its two acyloxy groups lying in approximately orthogonal planes. The α,β-unsaturated carbonyl

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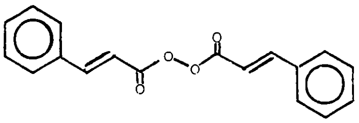
moiety has the *s-cis* stereochemistry, with a short C=O bond length indicative of minimal conjugation with the adjacent C=C bond.

Introduction. The structure of the title compound (1) was determined in continuation of our programme of work to relate diacyl peroxide structure and rates of thermolysis in solution and also to assist in the interpretation of polarized NMR spectra (CIDNP) by providing geometric data from which electron–nuclear hyperfine coupling constants in the related styryl radical might be estimated.



(1)

Experimental. (1) [m.p. 394–397 K (dec.)] prepared from *trans*-cinnamic acid and hydrogen peroxide in the presence of *N,N′*-dicyclohexylcarbodiimide (Greene & Kazan, 1963), suitable crystals obtained by recrystallization from methylene chloride/methanol; reflexion intensities measured by the SERC Microdensitometer Service, Daresbury Laboratory, from Weissenberg photographs of layers *hk*0 to *hk*4 from a section having dimensions 0·4 × 0·3 × 0·3 mm cut from a larger crystal, equivalents merged ($R_{\text{int}} = 0{\cdot}045$) giving 604 data used for structure determination and refinement, cell dimensions and interlayer scale factors determined from precession photographs using a second section cut from the same crystal; structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1970) in space group $P2_1$ and refined by full-matrix least squares on F (*XRAY72*; Stewart, Kruger, Ammon, Dickinson & Hall, 1972), ratio of least-squares shift-to-error in final refinement cycle = 0·0156 (max.) and 0·0024 (average); H atoms introduced at their calculated positions at an intermediate stage, but attempts to refine these positions using isotropic thermal parameters unsuccessful, for other atoms refinement with anisotropic thermal parameters; final $R = 0{\cdot}069$, unit weight; no extinction correction applied; max. and min. peak heights in final difference map 0·24 and –0·20 e Å^{-3} respectively.

Table 1. *Atomic coordinates* (×10^4) *and mean temperature factors* ($\bar{U}$) (×10^3) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}$(Å^2)
O(1)	3657 (8)	2601*	3897 (21)	64 (9)
O(2)	2506 (8)	3511 (22)	1541 (26)	75 (10)
C(3)	2755 (14)	2935 (26)	3306 (39)	37 (15)
C(4)	2247 (12)	2342 (30)	5287 (34)	64 (14)
C(5)	1345 (14)	2257 (26)	5076 (30)	61 (14)
C(6)	742 (14)	1587 (27)	6844 (34)	63 (14)
C(7)	–182 (15)	1658 (28)	6240 (31)	73 (17)
C(8)	–774 (12)	994 (30)	7649 (39)	68 (15)
C(9)	–461 (16)	311 (31)	9546 (41)	72 (17)
C(10)	435 (20)	186 (28)	10177 (36)	77 (17)
C(11)	1040 (13)	908 (28)	8789 (34)	64 (14)
O(12)	4247 (7)	3100 (21)	2140 (22)	62 (9)
O(13)	3879 (9)	1083 (23)	186 (25)	72 (10)
C(14)	4332 (12)	2093 (33)	384 (37)	57 (14)
C(15)	5103 (11)	2546 (27)	–967 (31)	54 (13)
C(16)	5343 (12)	1809 (26)	–2761 (31)	55 (13)
C(17)	6099 (12)	2022 (26)	–4309 (35)	49 (13)
C(18)	6674 (15)	3155 (30)	–4066 (37)	71 (16)
C(19)	7391 (14)	3286 (31)	–5629 (44)	86 (18)
C(20)	7473 (17)	2296 (41)	–7343 (36)	94 (20)
C(21)	6932 (19)	1112 (30)	–7531 (43)	80 (18)
C(22)	6260 (15)	1033 (29)	–6005 (39)	67 (16)

* This parameter was not refined.

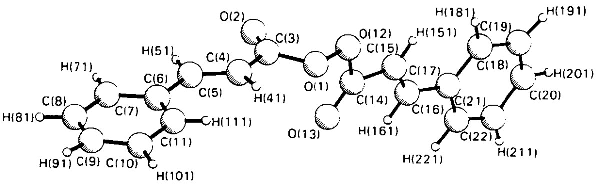


Fig. 1. A view of (1) drawn by *PLUTO* (Motherwell & Clegg, 1978).

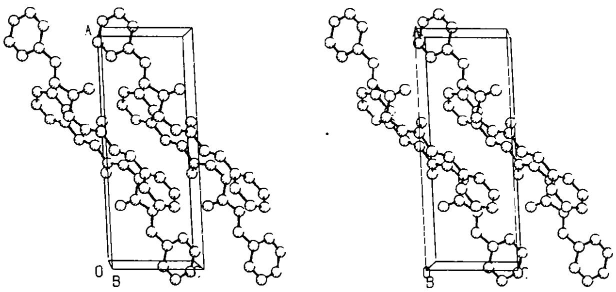


Fig. 2. Stereoscopic view of the crystal structure of (1) (drawn by *PLUTO*).

Discussion. Table 1 contains positional and mean isotropic thermal parameters for atoms other than H.* The molecular and crystal structures are shown in Figs. 1 and 2 respectively, and the atomic numbering, bond lengths, bond angles and torsion angles (not involving H) are in Fig. 3.

The molecule adopts an extended conformation in the crystal with the two cinnamoyl moieties essentially planar; the mean angles between the nodal planes of the carbonyl and phenyl groups in the two halves of the molecule are 4·5 and 11·5°. The two cinnamoyl groups lie in roughly orthogonal planes, however, since the

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* The corresponding data for the H atoms, together with lists of structure factors and anisotropic thermal parameters (for C and O atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39505 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

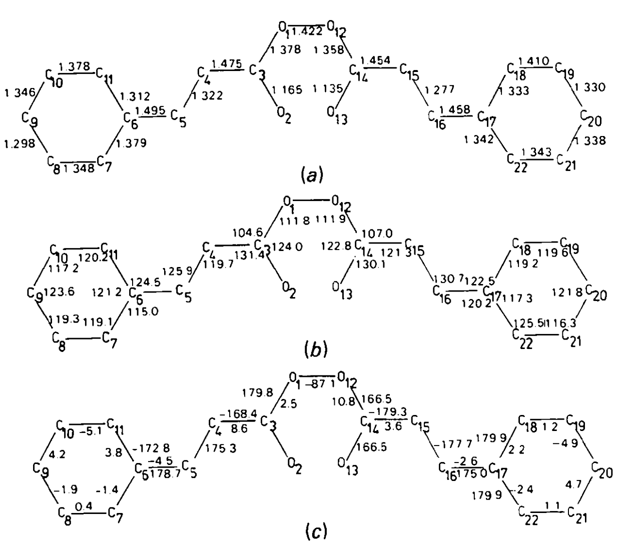

Fig. 3. (*a*) Bond lengths (Å), (*b*) bond angles (°), and (*c*) torsion angles (°) for (1). E.s.d.'s are 0·033 Å for bond lengths, 1·9° for bond angles and 2·0° for torsion angles. The ranges of bond lengths and angles involving H are C—H 0·886–0·952 Å, H—C—C 114·4–124·5°.

torsion angle about the O—O bond is 87·1°, a value close to that observed in five of the eight diacyl peroxide structures listed in the Cambridge Structural Database (1983) with $R \leq 0{\cdot}14$. The O—O bond length 1·42 (2) Å is somewhat shorter than the average for these eight compounds (1·458 Å).

We call attention to two other features of the present structure, namely the bond lengths in and the conformation of the α,β-unsaturated acyloxy groups. The carbonyl bond length is substantially shorter [mean value 1·15 (2) Å] than the average for the 13 compounds containing the cinnamoyl moiety for which structures having $R < 0{\cdot}10$ are available [1·228 (25) Å]. On the other hand it is little less than the average for the eight diacyl peroxides [1·186 (28) Å] which is itself less than is typical for unconjugated acyloxy groups [1·212 (4) Å] (Allen, 1981). The C=C bond lengths are close to the average for a cinnamoyl group. The overall picture is thus of strong conjugative interaction between the phenyl groups and their adjacent C=C bonds, but there seems to be little extension of the conjugation to the carbonyl groups despite the planarity.

In *trans*-cinnamoyl peroxide the α,β-unsaturated carbonyl group adopts the *s-cis* conformation. A review of gas-phase electron diffraction studies has led to the conclusion that the *s-trans* (or *anti*planar) conformation is favoured for sterically unhindered compounds at normal temperatures (Bohn, 1977), and this is also the case in almost half of the α,β-unsaturated acids for which crystal structures have been scrutinized (Einspahr & Donohue, 1973). Nevertheless, the *s-cis* conformation occurs in the majority of cases, especially in cinnamoyl compounds (see, for example, Hanson, 1975). In the present case there seems to be no obvious steric reason for the preference, and, in the absence of through conjugation, no strong electrostatic interaction either.

References

ALLEN, F. H. (1981). *Acta Cryst.* B**37**, 890–900.

BOHN, R. K. (1977). *Mol. Struct. Diffr. Methods*, **5**, 23–94.

CAMBRIDGE STRUCTURAL DATABASE (1983). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England. To be published as *Molecular Structures and Dimensions*, Vol. 15. Dordrecht: Reidel.

EINSPAHR, H. & DONOHUE, J. (1973). *Acta Cryst.* B**29**, 1875–1880.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B**26**, 274–285.

GREENE, F. D. & KAZAN, J. (1963). *J. Org. Chem.* **28**, 2168–2171.

HANSON, A. W. (1975). *Acta Cryst.* B**31**, 1963–1965.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY*72 system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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7-Methoxymethyl-12-methylbenz[*a*]anthracene, $C_{21}H_{18}O$

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Abstract. $M_r = 286{\cdot}4$, monoclinic, $P2_1/a$, $a = 7{\cdot}899\,(1)$, $b = 17{\cdot}041\,(3)$, $c = 11{\cdot}388\,(3)$ Å, $\beta = 99{\cdot}44\,(4)°$, $V = 1512{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}2$, $D_x = 1{\cdot}26$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}069$ mm^{-1}, $F(000) = 608$, $T = 298$ K, final $R = 0{\cdot}037$ for 1550 observed reflections. The planar anthracene skeleton is distorted around the attachment of the methyl group. The *K* region, C(5)—C(6), shows

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