Table 3. *Geometry of the hydrogen bonds with e.s.d.'s in parentheses*

D	H	A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)	Symmetry code
O(1)	H(O1)	N(1)	0·87 (3)	1·99 (4)	2·708 (3)	140 (3)	x, y, z
O(3)	H(O3)	O(4)	0·74 (3)	2·35 (2)	2·621 (2)	104 (2)	x, y, z
N(2)	H1(N2)	O(8)	0·92 (2)	2·03 (3)	2·708 (4)	129 (2)	x, y, z
O(3)	H(O3)	O(1)	0·74 (3)	2·03 (3)	2·744 (2)	161 (3)	$-x, -\tfrac{1}{2}+y, -z$
N(2)	H2(N2)	O(4)	0·99 (3)	2·30 (4)	3·167 (3)	145 (3)	$2-x, \tfrac{1}{2}+y, 1-z$

more than 30 norditerpenoid alkaloids have been determined and the absolute stereochemistry of some has been established (Joshi & Pelletier, 1987). The absolute configuration of delvestine is assumed by analogy with other alkaloids of this class.

References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, 24, 13–32.

BENN, M. H. & JACYNO, J. M. (1983). *Chemical and Biological Perspectives*, Vol. 1, edited by S. W. PELLETIER, pp. 153–210. New York: John Wiley.

DESAI, H. K., JOSHI, B. S. & PELLETIER, S. W. (1985). *Heterocycles*, 23, 2483–2487.

FRENZ, B. A. (1982). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

JOSHI, B. S. & PELLETIER, S. W. (1987). *Heterocycles*, 26, 2503–2518.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.

PELLETIER, S. W., DJARMATI, Z., LAJSIC, S. & DeCAMP, W. H. (1976). *J. Am. Chem. Soc.* 98, 2617–2625.

PELLETIER, S. W., JOSHI, B. S., GLINSKI, J. A., CHOKSHI, H. P., CHEN, S., BHANDARY, K. & GO, K. (1987). *Heterocycles*, 25, 365–376.

Structure of 2-*tert*-Butyl-3-phenyl-2-cyclopropenecarboxylic Acid

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Abstract. $C_{14}H_{16}O_2$, $M_r = 216\cdot28$, triclinic, $P\bar{1}$, $a = 8\cdot081$ (4), $b = 8\cdot390$ (3), $c = 10\cdot247$ (3) Å, $\alpha = 79\cdot70$ (2), $\beta = 81\cdot46$ (3), $\gamma = 72\cdot56$ (3)°, $V = 648\cdot8$ (5) Å^3, $Z = 2$, $D_x = 1\cdot11$ g cm^{-3}, λ(Mo $K\alpha$) = 0·709261 Å, $\mu = 0\cdot70$ cm^{-1}, $F(000) = 232$, $T = 293$ K, $R = 0\cdot056$ for 2780 observed reflexions. The *tert*-butyl group of the title compound does not affect the coplanar arrangement of the phenyl ring and the cyclopropene double bond. The carboxyl group possesses a bisected conformation relative to the cyclopropene ring. Of the two O atoms, the hydroxyl oxygen is nearer to the three-membered ring. This fact may explain the longer distances in the ring in comparison with the compound where the orientation of the carboxyl group is opposite [Korp, Bernal & Fuchs (1983). *Can. J. Chem.* 61, 50–56].

Introduction. According to Kobayashi, Arai, Sakuragi, Tokumaru & Utsunomiya (1981), the dihedral angle between the phenyl ring and the double bond in the molecules of cis-β-*tert*-butylstyrene is 72°. Thus, sterically bulky *tert*-butyl groups may exert a substantial influence on the position and on the conjugation of phenyl rings with double bonds. The molecule of 2-*tert*-butyl-3-phenyl-2-cyclopropenecarboxylic acid (I) contains the same fragment in a strained three-membered ring. The aim of the present communication is to answer the question whether the *tert*-butyl group will influence the spatial position of the phenyl group in compound (I).

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In the molecule of 2-methyl-3-phenyl-2-cyclo-propenecarboxylic acid, the phenyl and cyclopropene rings are coplanar, permitting maximum conjugation (Korp, Bernal & Fuchs, 1983).

Experimental. Crystals of compound (I) (Donaldson & Hughes, 1982) were obtained by slow evaporation from *n*-hexane solution (room temperature, two days). A crystal $0.5 \times 0.5 \times 0.4$ mm was used for all X-ray measurements. A Syntex $P2_1$ diffractometer (for automatic indexing and initial lattice parameters) and a Hilger & Watts Y290 diffractometer (for precise lattice parameters and intensity measurements) were used with graphite-monochromated Mo $K\alpha$ radiation. The cell parameters were determined by least-squares refinement of the setting angles of 20 reflexions within $34.4 \le 2\theta \le 45.8°$. Intensity data were measured by $\theta/2\theta$ scans ($4.5 \le 2\theta \le 60°$, $0 \le h \le 11$, $-11 \le k \le 11$, $-14 \le l \le 14$). There was no significant decay in the intensity for three standards monitored after every 97 reflexions. 4114 data were measured of which 3736 were symmetry independent ($R_{int} = 0.0153$). 2780 intensities were considered observed $[|F_o| > 4\sigma(F_o)]$. The data were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved by direct methods. All H atoms were localized in theoretical positions (sp^2 hybridization for benzene-type C atoms and sp^3 hybridization and staggered conformation for all other C atoms) except H(130) which was taken from a $\Delta\rho$ map. The structure was refined by full-matrix least-squares procedures on F, assigning anisotropic thermal displacement parameters to all non-H atoms. The refinements converged at $R = 0.056$ and $wR = 0.053$. The ratio of observations to the number of variables is greater than 13.5. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(|F_o|)$. Maximum shift/e.s.d. was 0.42 in final cycle; maximum and minimum heights in final $\Delta\rho$ map 0.17 and -0.25 e Å^{-3}. Complex neutral-atom scattering factors were taken from *SHELX*76. Programs used were *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976) and *PLATON*88 (Spek, 1982) on MicroVAX II and VAX 3200 computers.

Discussion. Final atomic parameters are given in Table 1, bond distances and angles are reported in Table 2.* Fig. 1 shows a view of the molecule and illustrates the atom-numbering scheme chosen.

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* Tables of structure factors, anisotropic thermal parameters, and H-atom positional and isotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52926 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{Å}^2)$
C(1)	0.0889 (2)	0.8187 (2)	0.2685 (1)	0.0551 (9)
C(2)	0.2775 (2)	0.8244 (2)	0.2292 (1)	0.0524 (8)
C(3)	0.2067 (2)	0.7827 (2)	0.1403 (1)	0.0539 (8)
C(11)	0.0520 (2)	0.6784 (2)	0.3667 (1)	0.0542 (8)
O(12)	−0.0848 (1)	0.7096 (2)	0.4471 (1)	0.0694 (6)
O(13)	0.1589 (2)	0.5312 (1)	0.3677 (1)	0.0686 (6)
C(21)	0.4189 (2)	0.8635 (2)	0.2843 (1)	0.0582 (8)
C(22)	0.5834 (2)	0.8368 (3)	0.1838 (2)	0.0722 (12)
C(23)	0.4609 (3)	0.7440 (4)	0.4151 (2)	0.0896 (15)
C(24)	0.3573 (4)	1.0487 (3)	0.3086 (3)	0.1010 (17)
C(31)	0.2026 (2)	0.7347 (2)	0.0117 (1)	0.0556 (8)
C(32)	0.0498 (3)	0.7182 (3)	−0.0239 (2)	0.0760 (12)
C(33)	0.0474 (3)	0.6725 (3)	−0.1479 (2)	0.0925 (13)
C(34)	0.1956 (3)	0.6422 (3)	−0.2349 (2)	0.0892 (13)
C(35)	0.3486 (3)	0.6561 (3)	−0.2006 (2)	0.0893 (13)
C(36)	0.3524 (3)	0.7017 (2)	−0.0776 (2)	0.0740 (11)

Table 2. *Selected bond lengths (Å) and angles (°)*

C(1)—C(2)	1.530 (2)	C(1)—C(3)	1.523 (2)
C(2)—C(3)	1.290 (2)	C(1)—C(11)	1.478 (2)
C(2)—C(21)	1.489 (2)	C(3)—C(31)	1.453 (2)
C(31)—C(32)	1.390 (3)	C(31)—C(36)	1.393 (3)
C(32)—C(33)	1.396 (3)	C(33)—C(34)	1.369 (3)
C(34)—C(35)	1.377 (4)	C(35)—C(36)	1.388 (3)
C(21)—C(22)	1.541 (3)	C(21)—C(23)	1.538 (3)
C(21)—C(24)	1.537 (3)	C(11)—O(12)	1.266 (2)
C(11)—O(13)	1.277 (2)		

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C(2)—C(1)—C(3)	50.0 (1)	C(2)—C(1)—C(11)	119.6 (1)
C(3)—C(1)—C(11)	120.3 (1)	C(1)—C(2)—C(3)	64.7 (1)
C(1)—C(2)—C(21)	139.7 (1)	C(3)—C(2)—C(21)	155.6 (2)
C(1)—C(3)—C(2)	65.3 (1)	C(1)—C(3)—C(31)	140.0 (2)
C(2)—C(3)—C(31)	154.8 (2)	C(3)—C(31)—C(32)	120.7 (2)
C(3)—C(31)—C(36)	120.7 (2)	C(32)—C(31)—C(36)	118.6 (2)
C(31)—C(32)—C(33)	120.1 (2)	C(32)—C(33)—C(34)	120.4 (2)
C(33)—C(34)—C(35)	120.2 (2)	C(34)—C(35)—C(36)	119.9 (2)
C(31)—C(36)—C(35)	120.7 (2)	C(2)—C(21)—C(22)	109.7 (1)
C(2)—C(21)—C(23)	108.8 (2)	C(2)—C(21)—C(24)	108.8 (2)
C(22)—C(21)—C(23)	109.3 (2)	C(22)—C(21)—C(24)	109.3 (2)
C(23)—C(21)—C(24)	110.9 (2)	O(12)—C(11)—O(13)	122.6 (1)
O(12)—C(11)—C(1)	118.4 (2)	O(13)—C(11)—C(1)	119.1 (1)
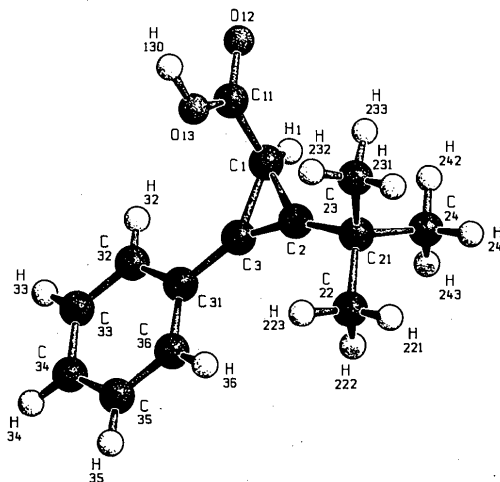
Fig. 1. *SCHAKAL*88 (Keller, 1986) drawing of the molecule $C_{14}H_{16}O_2$.

The principal structural difference between the double bond in open-chain olefins and the strained double bond in 1,2-disubstituted cyclopropenes is the angle formed between the substituent and the double bond. In olefins it is usually about 120°, but in cyclopropenes this angle increases to 151–155° (Allen, 1982; Domnin, Kopf, Keyaniyan & de Meijere, 1985). It turns out that this increase in angle is enough to ensure the same coplanar orientation of phenyl and cyclopropene rings in both compound (I) and in 2-methyl-3-phenyl-2-cyclopropenecarboxylic acid (Korp, Bernal & Fuchs, 1983). In general, the crystal and molecular structures of these compounds are similar, although in compound (I) the bond distances of the three-membered ring are longer. For C(1)—C(2) and C(2)—C(3) bonds this difference reaches 0·015 Å and for C(1)—C(3) 0·023 Å. The average phenyl-ring distances and the lengths of the bonds leading from the cyclopropene ring to the carbons of the carboxyl, phenyl and tert-butyl groups are also longer. The bond distances C—O in the carboxyl groups of both compounds are essentially the same. It is important to note that, although the carboxyl group also possesses the bisected conformation relative to the cyclopropene ring [corresponding dihedral angle 87·4 (1)°], the hydroxyl O atom is the O atom that is nearest to the three-membered ring, in contrast to the compound with the methyl substituent. Thus, one of the possible

explanations of the greater double-bond distance in compound (I) is the lack of interaction between the carbonyl group and the three-membered ring.

In the crystal structure of 2-tert-butyl-3-phenyl-2-cyclopropenecarboxylic acid, two molecules are combined by strong O—H···O hydrogen bonds forming dimers across the inversion center. The O···O separation is 2·657 (2), O···H is 1·681 (8) Å and the O—H···O angle is 174·7 (8)°.

References

ALLEN, F. R. (1982). Tetrahedron, 38, 645–655.
DOMNIN, I. N., KOPF, J., KEYANIYAN, S. & DE MEIJERE, A. (1985). Tetrahedron, 41, 5377–5382.
DONALDSON, W. A. & HUGHES, R. P. (1982). J. Am. Chem. Soc. 104, 4846–4859.
KELLER, E. (1986). Chem. Unserer Zeit, 20, 178–181.
KOBAYASHI, T., ARAI, T., SAKURAGI, H., TOKUMARU, K. & UTSUNOMIYA, C. (1981). Bull. Chem. Soc. Jpn, 54, 1658–1661.
KORP, J. D., BERNAL, I. & FUCHS, R. (1983). Can. J. Chem. 61, 50–56.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). SHELXS86. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
SPEK, A. L. (1982). PLATON88. In Computational Crystallography, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

Structure of 2,4,N-Trinitroanilinoacetic Acid

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Abstract. $C_8H_6N_4O_8$, $M_r = 286\cdot2$, monoclinic, $P2_1/n$, $a = 10\cdot417$ (1), $b = 10\cdot396$ (1), $c = 10\cdot880$ (1) Å, $\beta = 108\cdot61$ (1)°, $V = 1116\cdot6$ (2) Å^3, $Z = 4$, $D_m = 1\cdot68$, $D_x = 1\cdot70$ Mg m^{-3}, λ(Cu $K\alpha$) = $1\cdot5418$ Å, $\mu = 12\cdot46$ cm^{-1}, $F(000) = 584$, $T = 293$ K, final $R = 0\cdot040$ for 1374 unique reflections $[I \geq 3\sigma(I)]$. In the molecule the phenyl ring is slightly non-planar. The

oxygens of the carboxylic group dimerize across a centre of inversion forming hydrogen bonds with O—H···O distance 2·686 (3) Å and angle 172 (3)°.

Introduction. Aromatic amines and nitro compounds have a pivotal role in the synthetic chemistry of benzene. The nitro-group substitution results in a dramatic increase in the density of the compound. Several high-density nitro organics have been studied

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