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3-*E*-Benzylidene-1-t-butyl-2-oxo-4-*trans*-phenylcyclobutanecarbonitrile

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Abstract. $C_{22}H_{21}NO$, triclinic, $P\bar{1}$, $a=9{\cdot}824$ (6), $b=10{\cdot}799$ (1), $c=9{\cdot}622$ (6) Å, $\alpha=106{\cdot}74$ (2), $\beta=114{\cdot}60$ (8), $\gamma=83{\cdot}43$ (2)°, $Z=2$, $D_x=1{\cdot}172$ g cm^{-3}, $V=893{\cdot}7$ Å^3. The stereochemistry indicated in the title is demonstrated for the major product from the cycloaddition of diphenylallene and t-butylcyanoketen. Steric interactions between the bulky substituents lead to some abnormal bond lengths and angles.

Experimental. Measurements were made on a Nonius CAD-4 diffractometer using monochromatized Cu $K\alpha_1$ radiation ($\lambda=1{\cdot}54051$ Å). The cell dimensions and their e.s.d.'s were obtained by a least-squares fit of $\sin\theta$ values for 25 reflexions centred using the program *SETANG*. Intensities were recorded in the θ–2θ scan mode using a scintillation counter and pulse-height discrimination. The structure determination used the 3031 independent reflexions with $I>3\sigma(I)$, where $I=P-2(B_1+B_2)$ and $\sigma^2(I)=P+4(B_1+B_2)+(0{\cdot}05I)^2$. By this criterion 346 other reflexions with $\theta<70°$ were excluded as 'unobserved'. The structure was solved using the *MULTAN* programs (Main, Woolfson & Germain, 1971), with hydrogen atoms located on a subsequent difference synthesis. Least-squares refinement of atomic coordinates, anisotropic temperature factors for the heavy atoms and isotropic

Table 1. *Fractional coordinates and vibration parameters* (pm^2) *and their e.s.d.'s*

The temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}klb^*c^*)]$ or $\exp[-2\pi^2U_{iso}(2\sin\theta/\lambda)^2]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
C(1)	0·6203 (2)	0·7089 (2)	0·8248 (2)	296 (6)	335 (6)	459 (7)	59 (5)	202 (6)	−21 (5)
C(2)	0·5319 (2)	0·8386 (2)	0·8297 (2)	246 (6)	400 (6)	442 (7)	55 (6)	146 (5)	−5 (5)
C(3)	0·6111 (2)	0·8880 (2)	0·7555 (2)	245 (6)	409 (6)	404 (6)	87 (5)	154 (5)	27 (5)
C(4)	0·6829 (2)	0·7566 (2)	0·7174 (2)	241 (6)	358 (6)	365 (6)	43 (5)	140 (5)	−24 (5)
C(5)	0·7231 (2)	0·6930 (2)	0·9944 (2)	421 (7)	493 (7)	469 (7)	166 (6)	250 (6)	77 (6)
C(6)	0·8088 (2)	0·8172 (2)	1·0995 (2)	511 (9)	728 (11)	425 (8)	81 (8)	159 (7)	−62 (8)
C(7)	0·8334 (3)	0·5823 (2)	0·9879 (3)	799 (13)	712 (11)	707 (11)	366 (10)	428 (10)	359 (10)
C(8)	0·6219 (3)	0·6644 (2)	1·0683 (3)	732 (12)	751 (11)	715 (11)	276 (9)	471 (10)	24 (10)
C(9)	0·5231 (2)	0·5963 (2)	0·7331 (2)	411 (8)	426 (7)	616 (9)	45 (7)	294 (7)	−66 (6)
N(10)	0·4471 (2)	0·5096 (2)	0·6612 (2)	640 (10)	588 (9)	832 (11)	−36 (8)	352 (9)	−276 (8)
O(11)	0·4340 (2)	0·8781 (1)	0·8751 (2)	332 (5)	529 (6)	672 (7)	102 (5)	327 (5)	59 (5)
C(12)	0·6051 (2)	1·0069 (2)	0·7372 (2)	336 (7)	399 (7)	459 (7)	105 (6)	188 (6)	54 (5)
C(13)	0·6750 (2)	1·0626 (2)	0·6611 (2)	353 (7)	442 (7)	437 (7)	141 (6)	153 (6)	27 (6)
C(14)	0·6716 (3)	1·1956 (2)	0·6841 (3)	746 (11)	458 (8)	656 (10)	144 (8)	369 (9)	−10 (8)
C(15)	0·7349 (3)	1·2544 (2)	0·6142 (3)	1011 (16)	582 (10)	796 (13)	231 (9)	432 (12)	−131 (10)
C(16)	0·8014 (3)	1·1795 (2)	0·5185 (3)	681 (12)	943 (14)	648 (11)	361 (10)	257 (10)	−169 (10)
C(17)	0·8034 (2)	1·0480 (2)	0·4912 (2)	489 (9)	924 (13)	482 (8)	217 (9)	228 (8)	17 (9)
C(18)	0·7405 (2)	0·9888 (2)	0·5613 (2)	460 (8)	564 (8)	473 (8)	165 (7)	223 (7)	81 (7)
C(19)	0·8460 (2)	0·7411 (2)	0·7446 (2)	264 (6)	366 (6)	374 (6)	97 (5)	168 (5)	9 (5)
C(20)	0·9508 (2)	0·8380 (2)	0·8360 (2)	304 (6)	400 (7)	496 (7)	72 (6)	167 (6)	−30 (5)
C(21)	1·1007 (2)	0·8172 (2)	0·8606 (2)	297 (7)	587 (9)	588 (9)	133 (7)	161 (7)	−86 (6)
C(22)	1·1467 (2)	0·6997 (2)	0·7942 (2)	288 (7)	725 (10)	622 (9)	258 (8)	254 (7)	86 (7)
C(23)	1·0427 (2)	0·6037 (2)	0·6991 (2)	424 (8)	552 (8)	522 (8)	156 (7)	295 (7)	143 (7)
C(24)	0·8925 (2)	0·6245 (2)	0·6722 (2)	365 (7)	415 (7)	446 (7)	66 (6)	226 (6)	22 (6)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(4)	0·623 (2)	0·712 (2)	0·604 (2)	348 (35)	H(14)	0·615 (3)	1·250 (2)	0·752 (3)	687 (53)
H(12)	0·545 (2)	1·070 (2)	0·782 (2)	350 (36)	H(15)	0·731 (3)	1·358 (3)	0·638 (3)	978 (80)
H(61)	0·877 (3)	0·800 (2)	1·196 (3)	813 (64)	H(16)	0·837 (3)	1·224 (2)	0·462 (3)	778 (67)
H(62)	0·746 (3)	0·892 (3)	1·111 (3)	985 (71)	H(17)	0·849 (3)	0·989 (2)	0·425 (3)	722 (55)
H(63)	0·886 (3)	0·836 (2)	1·068 (2)	881 (63)	H(18)	0·739 (2)	0·899 (2)	0·542 (2)	562 (45)
H(71)	0·892 (3)	0·565 (2)	1·091 (3)	849 (69)	H(20)	0·916 (2)	0·925 (2)	0·880 (2)	508 (45)
H(72)	0·909 (3)	0·614 (2)	0·955 (3)	911 (64)	H(21)	1·172 (3)	0·882 (2)	0·921 (3)	736 (56)
H(73)	0·776 (2)	0·504 (2)	0·921 (3)	573 (49)	H(22)	1·255 (2)	0·685 (2)	0·815 (3)	578 (48)
H(81)	0·692 (3)	0·660 (2)	1·185 (3)	723 (61)	H(23)	1·072 (2)	0·518 (2)	0·650 (3)	592 (49)
H(82)	0·570 (3)	0·581 (3)	1·010 (4)	992 (78)	H(24)	0·822 (2)	0·557 (2)	0·609 (2)	458 (41)
H(83)	0·538 (3)	0·734 (2)	1·070 (3)	922 (67)					

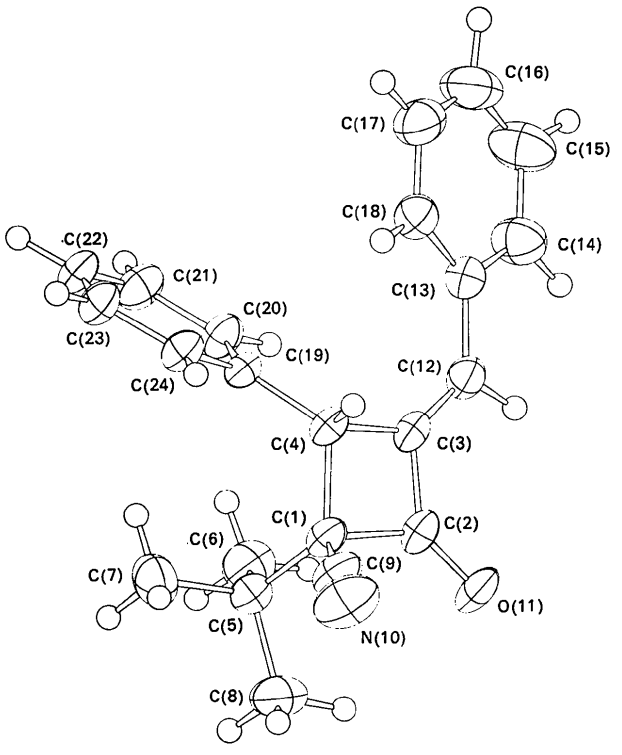

Fig. 1. *ORTEP* drawing of the molecule with atomic numbering.

temperature factors for the hydrogen atoms gave a final R of 6·11%. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1968) for C, N, and O, and from Stewart, Davidson & Simpson (1965) for hydrogen. The weights were derived from the expression for $\sigma^2(I)$ given above. The atomic coordinates and vibration parameters are given in Table 1*.

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

C(1)—C(2)	1·561 (2)	C(2)–C(1)—C(4)	85·8 (1)
C(2)—C(3)	1·471 (3)	C(2)–C(1)—C(5)	111·8 (1)
C(3)—C(4)	1·534 (2)	C(2)–C(1)—C(9)	113·1 (1)
C(4)—C(1)	1·614 (3)	C(4)–C(1)—C(5)	122·7 (1)
C(1)—C(5)	1·566 (2)	C(4)–C(1)—C(9)	110·9 (1)
C(1)—C(9)	1·466 (2)	C(5)–C(1)—C(9)	110·5 (1)
C(2)—O(11)	1·205 (2)	C(1)–C(2)—C(3)	92·5 (1)
C(3)—C(12)	1·334 (2)	C(1)–C(2)—O(11)	132·1 (1)
C(4)—C(19)	1·508 (2)	C(3)–C(2)—O(11)	135·3 (1)
C(5)—C(6)	1·531 (3)	C(2)–C(3)—C(4)	92·0 (1)
C(5)—C(7)	1·525 (3)	C(2)–C(3)—C(12)	127·3 (1)
C(5)—C(8)	1·538 (4)	C(4)–C(3)—C(12)	140·7 (2)
C(9)—N(10)	1·137 (2)	C(1)–C(4)—C(3)	88·3 (1)
C(12)–C(13)	1·457 (3)	C(1)–C(4)—C(19)	120·9 (1)
C(4)—H(4)	1·01 (2)	C(3)–C(4)—C(19)	122·7 (1)
C(12)–H(12)	0·98 (2)	C(3)–C(12)–C(13)	131·0 (2)
		C(1)–C(9)—N(10)	179·5 (2)

C–C(benzene ring)	1·372 (3)–1·398 (3),	mean = 1·386
C–H(benzene ring)	0·93 (2)—1·08 (3),	mean = 0·99
C–H(t-butyl group)	0·95 (2)—1·05 (3),	mean = 1·00

Discussion. This compound is the major product of the cycloaddition of diphenylallene and t-butylcyanoketen. The analysis was carried out to establish the stereochemistry (E or Z) about the benzylidene double bond, and to determine the relative configurations at carbon atoms (1) and (4). The mechanistic implications of the structure, which is shown in Fig. 1, were discussed in a preliminary communication (Bampfield, Brook, & McDonald, 1975) and will not be repeated here. The bond lengths and angles are listed in Table 2, and show some departures from normal values as a result of the steric interactions between the bulky substituents. The C(1)–C(4) bond between the mutually *cis* t-butyl and phenyl substituents has a length of 1·614 (3) Å, whilst the associated angles C(4)–C(1)–C(5), 122·7 (1)° and C(1)–C(4)–C(19), 120·9 (1)° are both substantially larger than the tetrahedral value. Similarly, the angles C(3)–C(4)–C(19), C(4)–C(3)–C(12), and C(3)–C(12)–C(13) are respectively 122·7 (1), 140·7 (2), and 131·0 (2)°, presumably a result of the steric interaction between the phenyl and benzylidene substituents. The cyclobutane ring is non-planar, with a dihedral angle of 11·9° about the C(2)···C(4) line, while the benzylidene substituent is also non-planar, with a dihedral angle of 13·7° between the mean planes of the phenyl ring and of the C(2), C(3), C(4), C(12), C(13), H(12) olefin group.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31134 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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