Remarquons enfin que la cohésion cristalline est assurée par trois liaisons hydrogène dans lesquelles l'ion Cl^- est engagé et par contacts de van der Waals (Fig. 4, Tableau 4).

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7-Methyl-3-methylenetricyclo[5.3.0.0^{1,4}]dec-5-yl Phenylcarbamate†

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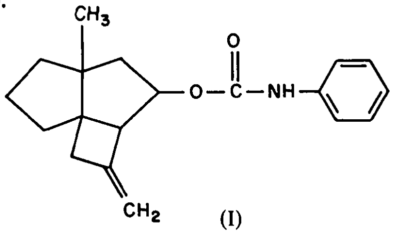
Abstract. $C_{19}H_{23}NO_2$, $M_r = 297 \cdot 40$, orthorhombic, $Pbcn$, $a = 15 \cdot 941$ (3), $b = 9 \cdot 739$ (3), $c = 22 \cdot 094$ (2) Å, $Z = 8$, $D_m = 1 \cdot 145$ (flotation in KI solution at 296 K), $D_c = 1 \cdot 152$ Mg m^{-3}, $\mu(\mathrm{Cu}\,K\alpha) = 0 \cdot 552$ mm^{-1}. Final $R = 0 \cdot 058$ and $R_w = 0 \cdot 059$ for 2143 observed reflexions. The two five-membered rings are *cis* fused as expected from the conformational preferences of the $n.\pi^*$ excited states of α,β-unsaturated ketones. Intermolecular N—H···O hydrogen bonds link the molecules into chains along **b**.

Introduction. The cycloaddition by photochemical reaction with dienes was studied extensively and proved to be important in the synthesis of alkaloids (Wiesner, Sanchez, Atwal & Lee, 1977). The crystal structure of a model compound of this reaction, obtained from an α,β-unsaturated ketone and an allene, and comprising two six-membered rings, was reported by Ahmed & Przybylska (1978). In addition, it was desirable to determine the stereochemistry of a tricyclic adduct containing two five-membered rings. The present phenylcarbamate derivative (I) was crystallized from *n*-hexane in the form of colourless prisms (m.p. 366–367 K).



(I)

The space group was determined from the systematic absences in precession photographs, and all the other X-ray measurements were carried out on a Picker diffractometer with Ni-filtered Cu radiation [$\lambda(K\alpha_1) = 1 \cdot 54050$, $\lambda(K\alpha_2) = 1 \cdot 54434$ Å] and a crystal $0 \cdot 39 \times 0 \cdot 39 \times 0 \cdot 22$ mm mounted along **b**. The cell parameters were derived from the angular settings of four reflexions ($2\theta = 58$ to $100°$) and their equivalents measured at 2θ and -2θ with a narrow slit at a take-off angle of 1·5°. The integrated intensities were obtained with the θ–2θ scan procedure at a 2θ speed of 2° min^{-1}, while the background was measured for 20 s at the start and end of each scan. The 2θ scan range was between 2·0 and 3·0°. Two reflexions measured at regular intervals showed small variations within ±3% of their mean values. Within the 2θ limit of 130° there were 2908 independent reflexions of which 2143 (74%) were observed with significant counts above background. The intensities were corrected for background, Lorentz and polarization effects, but not for absorption.

The phases of 640 reflexions with $|E| > 1 \cdot 20$ were determined by the symbolic-addition procedure (Karle & Karle, 1963), and the corresponding E map identified the positions of the 22 non-hydrogen atoms. After partial refinement, 22 of the 23 H atoms were located from a difference map. The missing H atom could not be observed even in the final difference map probably because of some minor disorder in the position of its parent C(2).

Refinement was by block-diagonal least squares, where $\sum w(F_o - F_c)^2$ was minimized and $w = \{1 + [(|F_o| - 20)/40]^2\}^{-1}$ in the final stages. Two very strong reflexions (302 and 212) showing extinction

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† NRCC publication No. 18353. The numbering in the title is according to IUPAC conventions and differs from that used throughout the text.

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were excluded from the final stages. In the final cycle, $R = 0{\cdot}058$ and $R_w = 0{\cdot}059$ for the observed reflexions, $[\sum w(\Delta F)^2/(m-n)]^{1/2} = 1{\cdot}00$, and the mean and maximum parameter shifts were 0·26 and 1·22 of their e.s.d.'s. Only four of the 765 unobserved reflexions were calculated above 1·5 times their threshold amplitudes. The final difference map showed a random distribution within −0·17 and 0·24 e Å^{-3}. Atomic parameters are listed in Table 1.[†] Calculations were carried out with the NRC program system (Ahmed, Hall, Pippy & Huber, 1973). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C, N, O, and of Stewart, Davidson & Simpson (1965) for H.

Table 1. *Fractional atomic coordinates* (×10^4 *for* C, N, O; ×10^3 *for* H) *and equivalent or isotropic temperature factors* (Å^2)

	x	y	z	B_{eq} or B
C(1)	3884 (3)	1915 (4)	3845 (2)	9·1
C(2)	3450 (4)	2234 (6)	3276 (2)	12·9
C(3)	3908 (3)	3416 (5)	2984 (2)	8·9
C(4)	4159 (2)	4258 (4)	3545 (1)	6·5
C(5)	3474 (2)	5248 (4)	3811 (1)	5·8
C(6)	3209 (2)	4617 (3)	4409 (1)	4·5
C(7)	3971 (2)	3872 (3)	4629 (1)	6·0
C(8)	4358 (2)	3240 (4)	4051 (2)	6·3
C(9)	4746 (2)	5513 (4)	3466 (2)	8·5
C(10)	4156 (2)	6368 (3)	3840 (2)	7·0
C(11)	4220 (3)	7547 (4)	4109 (2)	8·3
C(12)	5277 (3)	2927 (5)	4130 (2)	9·2
C(13)	2442 (2)	5332 (2)	5279 (1)	3·8
C(14)	1904 (2)	6431 (2)	6205 (1)	3·9
C(15)	2086 (2)	7494 (3)	6599 (1)	5·6
C(16)	1706 (2)	7537 (4)	7164 (1)	6·9
C(17)	1150 (2)	6545 (4)	7337 (1)	6·9
C(18)	966 (2)	5523 (3)	6943 (1)	6·7
C(19)	1330 (2)	5462 (3)	6375 (1)	5·1
N	2314 (1)	6428 (2)	5639 (1)	4·4
O(1)	2932 (1)	5709 (2)	4811 (1)	4·7
O(2)	2161 (1)	4198 (2)	5351 (1)	4·9
H(1,1)	436 (3)	121 (4)	382 (2)	12·8 (1·2)
H(1,2)	354 (2)	160 (4)	412 (1)	9·1 (1·0)
H(2,1)	343 (3)	139 (4)	300 (2)	14·1 (1·4)
H(3,1)	363 (2)	392 (3)	268 (1)	10·1 (1·0)
H(3,2)	439 (3)	262 (4)	287 (2)	11·3 (1·2)
H(5)	293 (2)	538 (3)	357 (1)	6·5 (0·7)
H(6)	276 (1)	401 (3)	431 (1)	5·0 (0·6)
H(7,1)	436 (2)	472 (3)	470 (1)	6·0 (0·7)
H(7,2)	385 (2)	315 (3)	497 (1)	9·6 (1·0)
H(9,1)	532 (2)	540 (3)	363 (1)	8·2 (0·8)
H(9,2)	478 (2)	580 (4)	305 (2)	11·5 (1·2)
H(11,1)	470 (2)	804 (3)	406 (1)	8·3 (0·9)
H(11,2)	377 (2)	787 (3)	433 (1)	9·4 (0·9)
H(12,1)	527 (3)	207 (4)	441 (2)	12·2 (1·2)
H(12,2)	555 (2)	381 (4)	421 (2)	12·0 (1·2)
H(12,3)	551 (2)	262 (3)	373 (1)	8·3 (0·9)
H(15)	250 (2)	809 (3)	648 (1)	5·8 (0·6)
H(16)	188 (2)	826 (3)	741 (1)	7·3 (0·8)
H(17)	87 (2)	657 (3)	773 (1)	7·8 (0·8)
H(18)	57 (2)	485 (3)	706 (1)	7·6 (0·8)
H(19)	119 (2)	471 (3)	610 (1)	7·0 (0·7)
H(N)	254 (2)	712 (2)	556 (1)	4·6 (0·5)

Discussion. Fig. 1 shows the stereochemistry of the tricyclic adduct. The two five-membered rings *A* and *B* are *cis* fused, and the side chain substituted at C(6) is equatorial. The structure agrees with the formulated conformational preference of the $n.\pi^*$ excited states of α,β-unsaturated ketones.

The bond lengths and angles, not corrected for thermal vibration, are presented in Fig. 2(*a*,*b*). The C(sp^3)—C(sp^3) lengths are in the range 1·468–1·570 Å, mean = 1·526 Å. The longest is C(4)—C(5) which is common to the four- and five-membered rings; the shortest is C(1)—C(2) which may be indicative of some disorder in the position of C(2), which also has a H atom missing (as frequently observed in five-membered rings). The $>$C(10)=C(11)H$_2$ length of 1·296 (5) Å is comparable to the corresponding lengths of 1·303 (5), 1·308 (6) and 1·310 (6) Å in the three independent molecules of $C_{14}H_{22}O$ (Ahmed & Przybylska, 1978). These lengths are closer to the mean value of 1·310 (5) Å of the partial triple bond in $H_2C{:}C{:}CH_2$ (allene) and $H_3C.CH{:}C{:}CH_2$ (methylallene) than to the mean value of 1·335 (5) Å of a simple $>$C=C$<$ double bond (Sutton, 1965). The O—C(=O)—NH chain linking rings *B* and *D* has a geometry similar to the corresponding chain in $C_{20}H_{25}N_3O_7S$ (Cameron, McElhatton, Campbell & Johnson, 1979) where the ratios $\Delta/(\sigma_1^2+\sigma_2^2)^{1/2}$ are within 1·3 for the bond lengths and within 2·2 for the

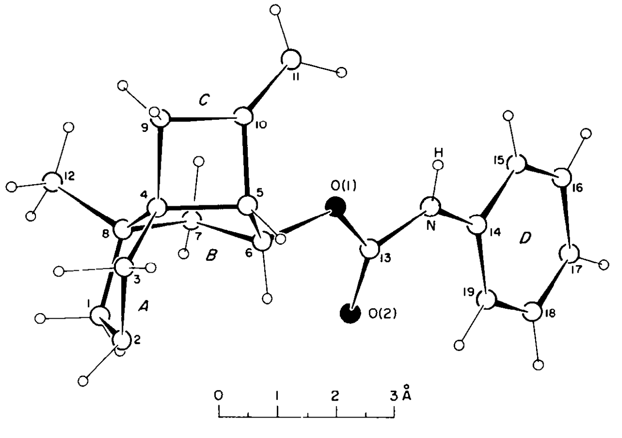

Fig. 1. Molecular drawing showing the stereochemistry and atom numbering.

[†] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35188 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

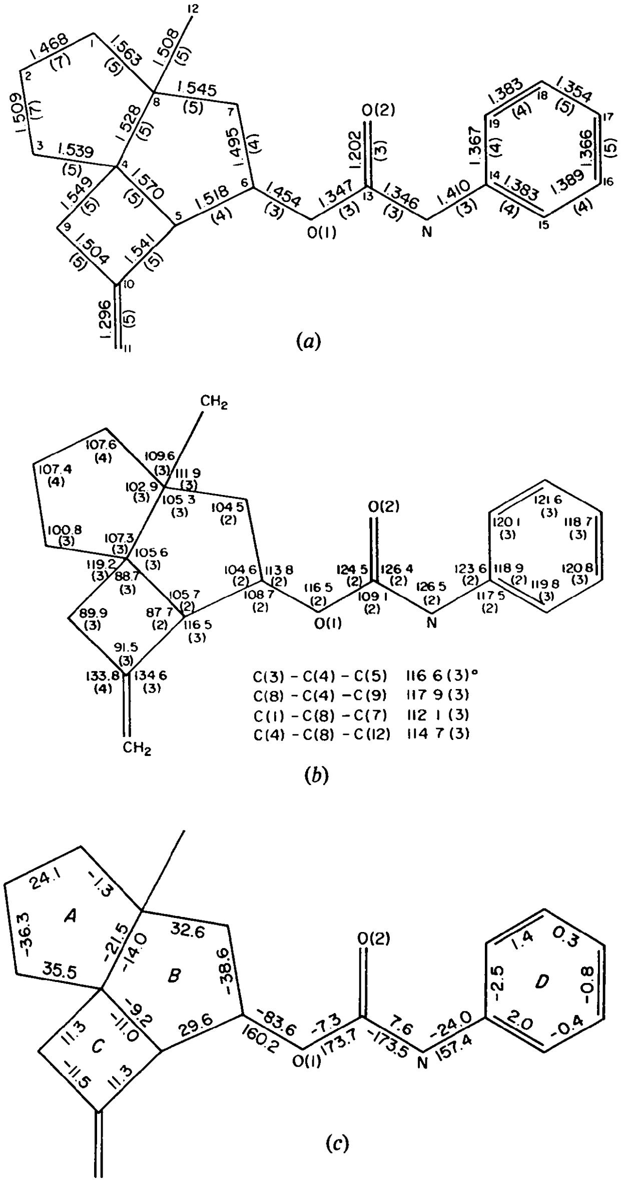

Fig. 2. (*a*) Bond lengths (Å); (*b*) valence angles (°); (*c*) torsion angles (°) ($\sigma \simeq 0{\cdot}4$–$0{\cdot}6°$).

angles. The overall $\chi^2 = \sum (\Delta/\sigma)^2$ for the three bond lengths and three angles is only 12·5. The mean endocyclic angle in each of the five-membered rings is 105·2 ± 0·1°, but the range of angles is much wider in ring *A* (100·8–107·6°) than in ring *B* (104·5–105·7°). The C—H lengths are 0·88–1·12 ($\sigma = 0{\cdot}03$–$0{\cdot}04$) Å, and N—H is 0·78 (2) Å.

The endocyclic and a few other torsion angles are presented in Fig. 2(*c*). Ring *A* adopts an envelope conformation with $\Delta C_s[C(3)] = 1{\cdot}9°$, while ring *B* has a half-chair conformation with $\Delta C_2[C(6)–C(7)] = 4{\cdot}0°$ (Duax, Weeks & Rohrer, 1976). Ring *C* is non-planar with its atoms within ±0·077 (4) Å from their mean plane. The dihedral angles between the three fused rings are *A–B* = 102·1, *A–C* = 96·0 and *B–C* = 72·5°, $\sigma \simeq 0{\cdot}5°$; the mean plane of ring *D* makes angles of 135·2, 76·9 and 40·2° ($\sigma \simeq 0{\cdot}5°$) with the mean planes of rings *A*, *B* and *C* respectively.

The only intermolecular contact shorter than van der Waals is O···H of a hydrogen bond linking the molecules into chains along **b**. The corresponding dimensions are O(2)···H(N′) = 2·13 (2), O(2)··N′ = 2·896 (3) Å and O(2)··H(N′)–N′ = 166 (2)°.

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