

**Discussion.** Les distances et les angles interatomiques de l'hétérocycle pentagonal et de son entourage sont groupés dans les Tableaux 2 et 3.

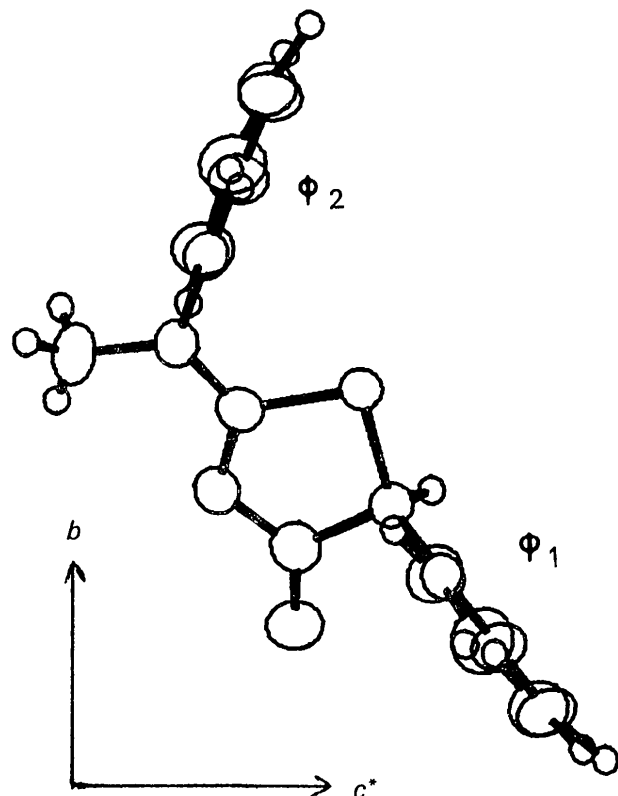


Fig. 3. Dispositions relatives des trois cycles atomiques dans la molécule.

Tableau 3. Principaux angles en degrés

C(1)—S—C(3)	89,7 (0,6)
S—C(1)—C(2)	104,9 (1,0)
S—C(1)—C(15)	115,0 (1,2)
C(2)—C(1)—C(15)	111,7 (1,3)
C(1)—C(2)—N(1)	115,5 (1,4)
C(1)—C(2)—O	119,9 (1,6)
O—C(2)—N(1)	124,6 (1,7)
C(2)—N(1)—C(3)	111,3 (1,4)
N(1)—C(3)—S	118,6 (1,3)
N(1)—C(3)—N(2)	123,1 (1,6)
N(2)—C(3)—S	118,4 (1,3)
C(3)—N(2)—C(16)	122,3 (1,7)
C(3)—N(2)—C(4)	120,3 (1,5)
C(4)—N(2)—C(16)	117,3 (1,6)

La Fig. 3, projection d'une molécule parallèlement à *a* (ORTEP, Johnson, 1965), rend compte de la disposition relative des 3 cycles atomiques: les cycles benzéniques  $\varphi_1$  et  $\varphi_2$  font entre eux un angle de  $59^\circ$  et respectivement avec le pentagone des angles de  $70^\circ$  et  $85^\circ$ .

Il n'y a pas de liaisons intermoléculaires fortes.

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## The Crystal Structure of 8-Phenyl-3,4,8-triaza-9-oxatricyclo[5,2,1,0<sup>2,6</sup>]dec-3-ene

BY TONY K. BRADSHAW, E. W. DELLA AND MAX R. TAYLOR

*School of Physical Sciences, The Flinders University of South Australia, Bedford Park, S.A. 5042, Australia*

(Received 14 May 1973; accepted 10 July 1973)

**Abstract.** C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 11.613 (3), *b* = 9.164 (3), *c* = 11.140 (3) Å,  $\beta$  = 117.375 (3)°, *Z* = 4, *D<sub>x</sub>* = 1.36, *D<sub>m</sub>* = 1.37 (1) g cm<sup>-3</sup>,  $\mu$  = 7.37 cm<sup>-1</sup>. Colourless crystals were obtained by crystallization from ether. Two-circle diffractometer data were refined to *R* = 0.043. The bridge-head angle of 92.3° is in good agreement with the gas phase value of 92° for norbornane.

**Introduction.** The systematic absences were *h*0*l* for *l* odd and 0*k*0 for *k* odd. The intensity data and unit-cell dimensions were measured on a Supper automatic two-circle equi-inclination diffractometer with nickel-

filtered Cu *K*α radiation. For each reflexion the optimum scan speed (to make the ratio  $\sigma(I)/I$  for all reflexions approximately the same) was estimated from an initial fast scan. The minimum and maximum scan ranges were 1.6° and 4° in  $\varphi$  and the scan speeds ranged from 0.025° sec<sup>-1</sup> to 0.33° sec<sup>-1</sup>. Further details of a similar diffractometer and its mode of operation are given by Freeman, Guss, Nockolds, Page & Webster (1970). One crystal, with dimensions 0.081 by 0.231 by 0.300 mm along *a*\*, *b*\*, and *c*\* respectively, was used to collect data from layers *k* = 0–6, and another, with dimensions 0.038 by 0.156 by 0.233 mm along *a*\*, *b*\*, and *c*\* respectively, to collect

layers  $l=0-7$ . Absorption corrections were calculated and applied (de Meulenaer & Tompa, 1965). The data were scaled by the method of Rae (1965) to give intensities for a set of 1867 independent reflexions, of which 442 had an intensity that was less than 2.5 standard deviations above background. The latter were given a theoretical value and standard deviation according to Hamilton (1955), but were excluded from the least-squares refinement. Standard deviations for the other reflexions were calculated from a combination of counting statistics and mean deviations for those intensities measured more than once (41% of the data), and counting statistics alone for the remainder.

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by full-matrix least-squares calculations minimizing  $\sum w(\Delta F)^2$  where  $w = \sigma^{-2}(F_o)$ . All hydrogen atoms were located in a difference map. In the final

refinement cycles a scale factor, positional parameters for all atoms, anisotropic temperature factor coefficients for non-hydrogen atoms, and individual isotropic temperature factors for hydrogen atoms (197 parameters) were refined. The refinement was terminated when all the shifts had fallen to less than one-third of their estimated standard deviations. The final *R* indices were 0.062 for the complete data set and 0.043 for the data used in the refinement. The atomic scattering factors for C, N, and O were taken from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). Final atomic parameters are listed in Table 1(a) and (b).\*

\* A table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30176 (11 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

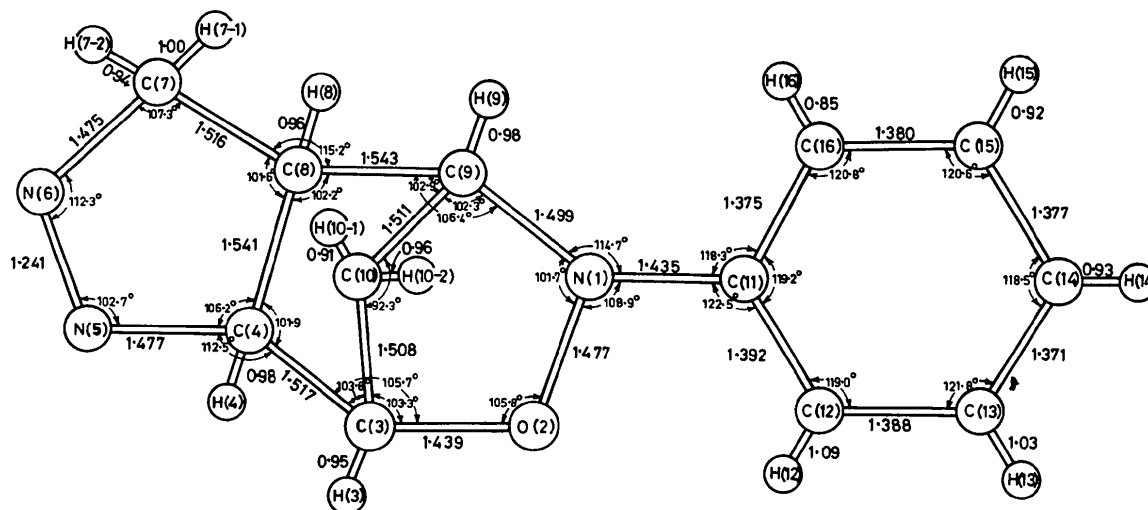


Fig. 1. Interatomic distances and angles in the molecule. Standard deviations in interatomic distances are 0.03 Å for bonds involving hydrogen atoms, 0.003 Å for others, and 0.02° in angles. Angles involving hydrogen atoms are not shown.

Table 1. *The final atomic parameters*

(a) Non-hydrogen atoms

$$\text{Temperature factor} = \exp [ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) ] .$$

All values are  $\times 10^4$ . Standard deviations are in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
N(1)	5960 (2)	2473 (2)	2052 (2)	63 (2)	87 (3)	84 (2)	3 (2)	41 (2)	0 (2)
O(2)	6293 (2)	1412 (2)	1260 (2)	86 (2)	90 (3)	145 (2)	4 (2)	73 (2)	-8 (2)
C(3)	7015 (2)	2238 (3)	720 (3)	79 (2)	119 (4)	101 (3)	-2 (3)	57 (2)	-16 (3)
C(4)	8348 (2)	2460 (3)	1900 (3)	71 (2)	94 (4)	113 (3)	14 (3)	47 (2)	10 (3)
N(5)	9257 (2)	3162 (3)	1489 (2)	71 (2)	154 (4)	137 (3)	6 (2)	60 (2)	6 (3)
N(6)	9557 (2)	4422 (3)	1942 (2)	81 (2)	143 (4)	163 (3)	-11 (3)	62 (2)	-3 (3)
C(7)	8911 (3)	4863 (4)	2750 (4)	83 (3)	154 (6)	156 (5)	-26 (3)	57 (3)	-37 (4)
C(8)	8069 (2)	3600 (3)	2753 (2)	64 (2)	135 (5)	81 (3)	-2 (3)	31 (2)	-7 (3)
C(9)	6604 (2)	3837 (3)	1910 (2)	63 (2)	84 (4)	94 (3)	6 (2)	41 (2)	-6 (3)
C(10)	6405 (2)	3712 (3)	471 (2)	67 (3)	115 (5)	88 (3)	3 (3)	35 (2)	26 (3)
C(11)	4576 (2)	2564 (2)	1489 (2)	67 (2)	73 (3)	73 (3)	1 (2)	40 (2)	9 (2)
C(12)	3743 (2)	1716 (3)	398 (3)	77 (3)	121 (5)	102 (3)	-12 (3)	46 (2)	-24 (3)
C(13)	2418 (3)	1821 (3)	-56 (3)	76 (3)	168 (5)	111 (3)	-22 (3)	35 (3)	-27 (3)
C(14)	1905 (3)	2750 (3)	550 (3)	63 (3)	149 (5)	119 (4)	2 (3)	46 (3)	8 (3)
C(15)	2738 (3)	3578 (3)	1621 (3)	88 (3)	135 (5)	118 (3)	16 (3)	70 (3)	6 (3)
C(16)	4061 (2)	3487 (3)	2101 (3)	76 (3)	129 (4)	83 (2)	-3 (3)	45 (2)	-13 (3)

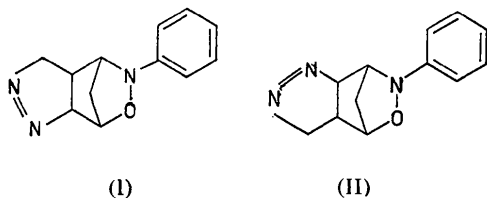
Table 1 (cont.)

(b) Hydrogen atoms

Temperature factor =  $\exp(-B \sin^2 \theta/\lambda^2)$ .Positional parameters are  $\times 10^3$ . Standard deviations are in parentheses.

	x	y	z	B, Å <sup>2</sup>
H(3)	696 (2)	166 (3)	-7 (2)	4.0 (6)
H(4)	871 (2)	156 (3)	232 (2)	3.5 (6)
H(7-1)	836 (3)	576 (4)	218 (3)	7.7 (1.0)
H(7-2)	955 (3)	525 (3)	363 (3)	6.2 (8)
H(8)	828 (2)	328 (2)	371 (2)	3.4 (6)
H(9)	627 (2)	464 (2)	222 (2)	2.7 (5)
H(10-1)	684 (2)	446 (3)	27 (2)	4.4 (7)
H(10-2)	549 (2)	377 (3)	-15 (2)	3.7 (6)
H(12)	416 (2)	102 (3)	-3 (3)	4.8 (6)
H(13)	186 (2)	133 (3)	-95 (3)	5.1 (7)
H(14)	102 (2)	283 (3)	29 (2)	4.3 (6)
H(15)	245 (2)	426 (3)	204 (2)	3.6 (6)
H(16)	461 (2)	405 (3)	278 (2)	3.2 (6)

**Discussion.** Treatment of 3-phenyl-2-oxa-3-azabicyclo[2,2,1]hept-5-ene (Kresze & Schulz, 1961) with diazomethane in ether at  $-10^\circ\text{C}$  gives a colourless solid which can be separated into two crystalline forms by fractional crystallization from ether (Bradshaw, Bruer & Della, unpublished results). Half the mixture consists of crystalline plates, the other half, of needle-shaped crystals. Nuclear magnetic resonance, mass spectrometry, and other spectroscopic techniques, although showing that the two crystalline forms were distinct isomers, proved inadequate in distinguishing between the structural isomers (I) and (II), both of which presumably arise from *exo* addition of diazomethane (Brown, 1972).



A preliminary X-ray examination showed the plates to be of better quality than the needles so the former

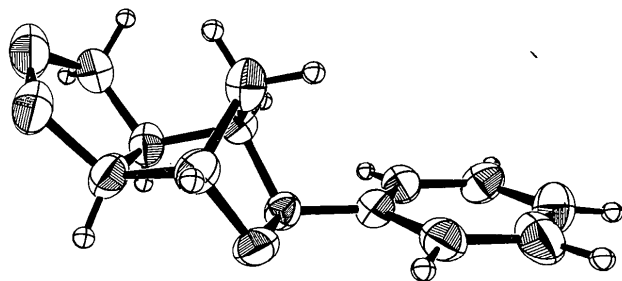


Fig. 2. A perspective view of the molecule showing thermal ellipsoids drawn at the 50% probability level for all atoms except hydrogen which are arbitrary spheres (Johnson, 1965).

were chosen for this study to determine the structure of one of the isomers unequivocally. The plates were shown to be isomer (I). Bond lengths and bond angles are shown in Fig. 1 and the conformation of the molecule with thermal ellipsoids in Fig. 2.

Conformation of the norbornane-type bridge-ring system is in agreement with the results of previous work such as the structure of *anti*-7-norbornenyl-*p*-bromobenzoate by Macdonald & Trotter (1965), where most of the bond lengths and angles are nearly identical with those reported here. Of particular interest is the value of the bridgehead angle, C(3)-C(10)-C(9), which differs significantly from the tetrahedral value, as with similar bridged molecules. The value obtained here ( $92.3^\circ$ ) is similar to that obtained for norbornane in the gas phase ( $92.0 \pm 0.8^\circ$ ) by Morino, Kuchitsu & Yokozochi (1967). The values reported by Macdonald & Trotter (1965) are significantly higher for similar molecules.

Bond distances and valency angles in the five-membered diazo ring and the phenyl group are all normal. The atoms O(2)-N(1)-C(11)-C(12)-H(12) are essentially coplanar, the maximum deviation from the least-squares plane through these atoms being 0.02 Å. The strain resulting from the close proximity of O(2) and H(12) (2.29 Å) is evidently more than compensated by the delocalization of electrons over O(2), N(1), and the aromatic ring.

T.K.B. wishes to thank the Commonwealth of Australia for a Postgraduate Award and Mrs Lata Prasad for her assistance during the latter stages of this analysis. The operation of the diffractometer is, in part, supported by Grant C66/16087 from the Australian Research Grants Committee.

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