

is  $N \cdots O(2^1) = 2.94 \text{ \AA}$ . This clearly corresponds to a hydrogen bond with  $N-H(N) 0.79 \text{ \AA}$  and  $H(N) \cdots O(2^1) 2.18 \text{ \AA}$ . Similar values were found between the glutarimido residuals in thalidomide (Allen & Trotter, 1970) where  $N \cdots O$  is  $2.93 \text{ \AA}$ ,  $N-H(N) 0.82 \text{ \AA}$  and  $H(N) \cdots O 2.12 \text{ \AA}$ . The molecules, connected by hydrogen bonds, form roof-like ribbons running along  $c$ . The average planes of the ribbons are parallel (100) and the packing distance of the ribbons is  $3.38 \text{ \AA}$ .

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## Tetracyclo[5,2,1,0<sup>2,6</sup>,0<sup>4,9</sup>]decan-3-one-2,4-dinitrophenylhydrazone

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**Abstract.** Triclinic,  $P\bar{1}$ ,  $a = 7.160$  (8),  $b = 11.066$  (7),  $c = 10.612$  (14)  $\text{\AA}$ ,  $\alpha = 81.77$  (5),  $\beta = 63.38$  (6),  $\gamma = 80.33$  (5)°,  $C_{16}H_{16}O_4N_4$ ,  $Z = 2$ ,  $D_o = 1.473$  (14),  $D_c = 1.476 \text{ g cm}^{-3}$ . The compound contains a distorted boat cyclohexane ring with a short  $1.90$  (5)  $\text{\AA}$   $H \cdots H$  contact. Endocyclic bond angles within the strained tetracyclo fragment ( $94.3$  to  $108.4^\circ$ ) are all less than the tetrahedral angle; C–C(cage) single-bond distances range from  $1.497$  to  $1.583 \text{ \AA}$  (mean  $1.541 \text{ \AA}$ ).

**Introduction.** Crystals of the parent compound (VI, Fig. 1) (Sauers & Henderson, 1974) proved unaccept-

able for X-ray analysis. The 2,4-dinitrophenylhydrazone derivative was readily prepared and thin hexagonally shaped crystals were grown from ethanol/ethyl acetate solutions (m.p.  $192$ – $193.5^\circ\text{C}$ ). A single crystal, cut to  $0.6 \times 0.3 \times 0.07 \text{ mm}$ , was used. Preliminary Weissenberg photographs showed no systematic absences. Intensities were collected on a CAD-3 automated diffractometer ( $\theta$ – $2\theta$  scan) with Ni-filtered  $\text{Cu } K\alpha$  radiation. Of the 2499 unique reflections measured ( $4 < 2\theta < 130^\circ$ ), 1734 with  $F^2 \geq 2\sigma$  (counting statistics) were considered observed, and used in the structure solution and refinement. Absorption corrections were not applied ( $\mu$  for  $\text{Cu } K\alpha = 9.19 \text{ cm}^{-1}$ ).

The structure, assumed to be centrosymmetric, was solved by reiterative application of Sayre's equation using 312 reflections with  $|E| \geq 1.5$  and a program developed by Long (1965). In addition to the origin-defining reflections, the phases of five reflections were arbitrarily assigned, leading to 32 possible solutions. The true solution required the fewest iterations (two) for phase convergence, had approximately equal numbers of positive and negative phases ( $149+$ ,  $163-$ ), and showed the second highest value of the consistency index  $c = \langle |E_A \sum_{A=B+C} E_B E_C| \rangle / \langle |E_A| \sum_{A=B+C} |E_B| |E_C| \rangle$ . All

C, N and O atoms were located from an  $F$  map based on these 312 phases; the computer programs used have been described (Potenza, Giordano, Mastropaolo & Efraty, 1974). Scattering factors for H were taken from *International Tables for X-ray Crystallography* (1962) and for C, N and O from Cromer & Waber (1965). After five cycles of full-matrix refinement, the last two with anisotropic thermal parameters, 14 of the 16 H atoms were located on a difference map. After an ad-

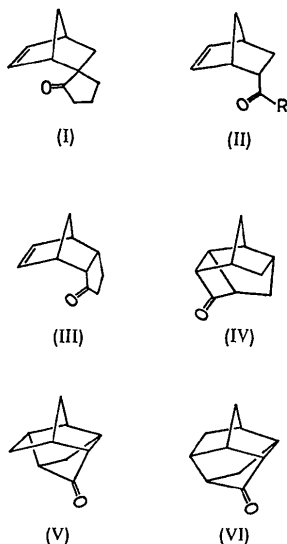


Fig. 1. Structures of compounds mentioned in the text.

ditional cycle, the remaining two H atoms were located similarly. For the final cycles, weights  $w=1/\sigma^2$  were determined by an analysis of variance to make  $\Delta F/\sigma$  independent of  $F_o$ . This led to the following assignments:  $\sigma(F_o)=2.04-0.135|F_o|$  for  $|F_o|\leq 9.92$ ,  $\sigma(F_o)=0.973-0.012|F_o|$  for  $9.92<|F_o|<20.3$  and  $\sigma(F_o)=0.465+0.018|F_o|$  for  $|F_o|\geq 20.3$ . The final value of  $R_F$  was 0.0520 while  $R_{wF}=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}$ , the quantity minimized, was 0.059.\* A final difference map showed no extraneous peaks. Atomic parameters are shown in Table 1 and a sketch of the molecule in Fig. 2.

**Discussion.** In contrast to the behavior of (I) (Fig. 1) and of numerous derivatives of (II) whose photolysis led to oxetane derivatives, (III), under similar conditions, yielded as the major product (85%) a ketone whose structure could be formulated either as (IV), (V) or (VI). Since attempts to characterize the product unambiguously by chemical degradation and spectroscopic methods were unsuccessful (Henderson, 1973), an X-ray structure determination was undertaken. The results clearly indicate that ketone (VI), which may be regarded as being composed of a norbornane part [C(10)–C(16)] and a 7-norbornanone part [C(7)–C(13)] with four atoms in common, is correct. The mechanistic and photochemical implications of this result have been presented elsewhere (Sauers & Henderson, 1974).

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30989 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Within the tetracyclo fragment, C–C distances vary from 1.497 to 1.583 Å, a range somewhat larger (*ca* 0.03 Å) than that typically found for norbornane derivatives (Altona & Sundaralingam, 1972), 7-norbornanone (Li, 1971), and several polycyclic cage hydrocar-

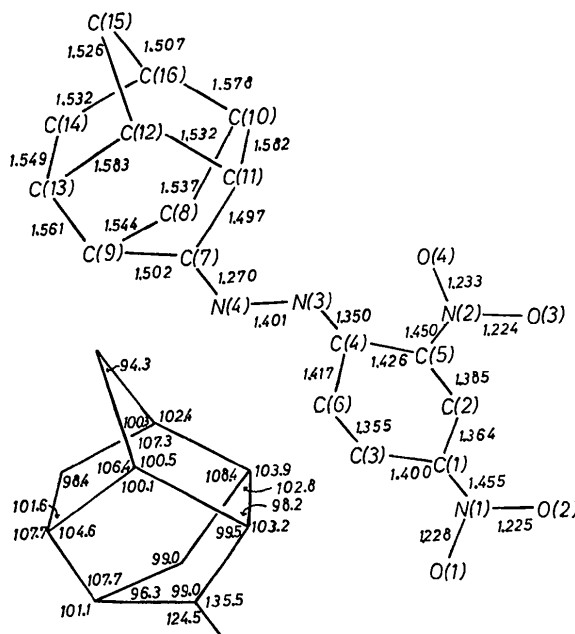


Fig. 2. Sketch of the molecule showing the numbering scheme, bond distances (Å) and selected angles (°). Average e.s.d.'s are: O–N 0.003; N–N 0.002; C–N 0.003; C–C 0.004 Å; C–C–C 0.3°.

Table 1. Final atomic parameters

Estimated standard deviations obtained from the least-squares refinement are given in parentheses. Coordinates and  $\beta$  values are  $\times 10^4$ . The expression for the anisotropic thermal parameters is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O(1)	6585 (4)	-5654 (2)	-4371 (3)	447 (8)	52 (2)	179 (4)	-25 (3)	-87 (5)	-17 (2)
O(2)	9272 (4)	-5031 (2)	-6208 (2)	389 (7)	79 (2)	115 (3)	46 (3)	-74 (4)	-45 (2)
O(3)	10646 (4)	-913 (2)	-6921 (2)	231 (6)	101 (2)	97 (3)	-34 (3)	29 (3)	-27 (2)
O(4)	8476 (3)	488 (2)	-5619 (2)	226 (5)	58 (2)	99 (3)	-21 (3)	-38 (3)	-5 (2)
N(1)	7668 (4)	-4847 (2)	-5118 (3)	302 (7)	58 (2)	106 (3)	11 (3)	-91 (4)	-2 (2)
N(2)	9004 (2)	-592 (2)	-5910 (2)	169 (5)	64 (2)	70 (3)	-13 (3)	-34 (3)	-9 (2)
N(3)	5185 (3)	-99 (2)	-3268 (2)	165 (5)	47 (2)	67 (3)	-13 (3)	-12 (3)	-18 (2)
N(4)	3460 (3)	33 (2)	-1948 (2)	172 (5)	51 (2)	76 (3)	-11 (3)	-23 (3)	-21 (2)
C(1)	6998 (4)	-3595 (3)	-4686 (3)	237 (7)	44 (2)	81 (3)	7 (3)	-65 (4)	-17 (2)
C(2)	8248 (4)	-2697 (3)	-5444 (3)	187 (6)	62 (2)	63 (3)	16 (3)	-41 (4)	-25 (2)
C(3)	5106 (5)	-3344 (3)	-3490 (3)	241 (7)	58 (3)	89 (4)	-27 (4)	-45 (4)	-12 (2)
C(4)	5775 (4)	-1219 (2)	-3778 (3)	153 (5)	48 (2)	66 (3)	2 (3)	-52 (3)	-12 (2)
C(5)	7646 (4)	-1510 (2)	-5023 (3)	151 (6)	52 (2)	56 (3)	-6 (3)	-36 (3)	-8 (2)
C(6)	4529 (5)	-2189 (3)	-3053 (3)	192 (7)	57 (3)	85 (4)	-12 (4)	-21 (4)	-20 (2)
C(7)	3184 (4)	1040 (3)	-1411 (3)	154 (6)	52 (2)	74 (3)	-11 (3)	-33 (4)	-11 (2)
C(8)	494 (5)	2566 (3)	-601 (3)	195 (7)	84 (3)	112 (4)	16 (4)	-38 (5)	-26 (3)
C(9)	1447 (4)	1397 (3)	-13 (3)	172 (6)	58 (2)	73 (3)	-14 (3)	-16 (4)	-24 (2)
C(10)	2458 (5)	3247 (3)	-1360 (3)	243 (7)	47 (2)	107 (4)	9 (3)	-77 (4)	-13 (2)
C(11)	4314 (4)	2159 (3)	-1823 (3)	173 (6)	48 (2)	77 (3)	-14 (3)	-18 (4)	-17 (2)
C(12)	4883 (5)	2098 (3)	-583 (3)	203 (7)	70 (3)	114 (4)	-4 (4)	-72 (4)	-16 (2)
C(13)	2715 (5)	1811 (3)	693 (3)	234 (8)	78 (3)	77 (4)	3 (4)	-45 (4)	-22 (2)
C(14)	1712 (5)	3112 (3)	1195 (3)	312 (9)	99 (3)	105 (4)	-6 (4)	-61 (5)	-59 (2)
C(15)	5050 (5)	3451 (3)	-567 (4)	285 (8)	85 (3)	149 (5)	-28 (4)	-88 (5)	-38 (3)
C(16)	2764 (5)	3859 (3)	-220 (4)	267 (8)	54 (3)	161 (5)	15 (4)	-92 (5)	-47 (2)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	C-H (Å)
H(N3)	5926 (44)	486 (30)	-3696 (29)	1.7 (7)	0.88 (3)
H(C2)	9424 (43)	-2818 (28)	-6227 (30)	1.6 (7)	0.91 (2)
H(C3)	4146 (44)	-4009 (29)	-3003 (31)	1.6 (7)	0.99 (3)
H(C6)	3234 (42)	-2033 (28)	-2289 (29)	1.1 (7)	0.93 (2)
H(1C8)	-91 (54)	2289 (36)	-1252 (38)	4.5 (10)	1.10 (5)
H(2C8)	-670 (46)	3040 (31)	113 (32)	2.3 (8)	0.98 (3)
H(C9)	362 (40)	817 (26)	555 (28)	0.6 (6)	0.99 (3)
H(C10)	2366 (44)	3818 (29)	-2094 (30)	1.7 (8)	0.94 (3)
H(C11)	5420 (39)	2332 (27)	-2830 (27)	0.7 (6)	1.00 (2)
H(C12)	5909 (45)	1546 (31)	-655 (31)	1.7 (7)	0.91 (3)
H(C13)	2798 (44)	1149 (29)	1359 (31)	1.5 (7)	0.96 (3)
H(1C14)	81 (44)	3237 (30)	1536 (31)	1.6 (8)	1.04 (3)
H(2C14)	2241 (50)	3225 (33)	1937 (34)	3.0 (9)	0.98 (5)
H(1C15)	5941 (55)	3875 (37)	-1634 (38)	4.3 (10)	1.09 (3)
H(2C15)	5455 (58)	3565 (37)	293 (38)	4.7 (11)	1.07 (6)
H(C16)	2439 (46)	4758 (30)	-316 (31)	1.7 (7)	0.97 (3)

bons (Rao & Sundaralingam, 1972). However, the mean C-C distance, 1.541 Å, compares favorably with those of the above structures. The shortest distances are those involving the bridging atoms C(7) and C(15). The six-membered ring [C(8)-C(9)-C(13)-C(14)-C(16)-C(10)] is forced into a distorted boat configuration which gives rise to a short intramolecular H...H contact [H(2C8)...H(1C14) 1.90 (5) Å]. No remaining non-geminal H...H contacts are substantially shorter than the van der Waals diameter (*ca* 2.4 Å).

Endocyclic C-C-C bond angles (94.3 to 108.4°) are all smaller than the tetrahedral angle and suggest substantial ring strain, as expected. The respective bridge

angles [C(12)-C(15)-C(16) 94.3; C(9)-C(7)-C(11) 99.0°] compare well with the average of 94.2° for norbornane and several derivatives, and with the value of 99.5° for 7-norbornanone. Structural parameters for the 2,4-dinitrophenylhydrazono group appear typical (Menczel, Samay & Simon, 1972).

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