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Methyl 4-(2-Furyl)-6,8-dioxo-2,7-diphenyl-3,7-diazabicyclo[3.3.0]octane-2-carboxylate

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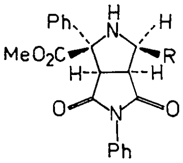
Abstract. $C_{24}H_{20}N_2O_5$, M_r = 416·4, triclinic, $P\bar{1}$, a = 10·376 (1), b = 13·276 (2), c = 14·655 (2) Å, α = 98·71 (2), β = 95·26 (1), γ = 93·20 (1)°, U = 1982·1 Å^3, Z = 4, D_x = 1·39 Mg m^{-3}. The two independent molecules in the asymmetric unit display very similar geometries although there are some differences in the orientations of the substituent groups on the diazabicyclooctane ring system.

Introduction. The synthesis of the title compound (I) has been described previously (Grigg, Kemp, Sheldrick & Trotter, 1978). Good-quality crystals were obtained by recrystallization from methylene chloride/petrol and a crystal *ca* 0·12 × 0·13 × 0·37 mm was selected for data collection. Intensity measurements were made on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Reflexions with $I < \sigma_I/2$ on a prescan (prescan speed 3·3° min^{-1}) were not remeasured: the remaining reflexions were scanned again in both forward and reverse directions at slower speeds determined by the prescan, a maximum of 60 s being allowed for each reflexion. From analyses of peaks an ω–θ scan and an ω-scan range of (1·0 + 0·35 tan θ)° were found suitable. All unique reflexions were measured in the range 1·0 ≤ θ ≤ 20·0°. An intensity-control reflexion recorded every 5000 s showed no significant variation in intensity. Cell dimensions were calculated from the diffractometer settings of 25 high-angle reflexions. Lp but no absorption corrections were applied (μ = 0·06 mm^{-1}). 2434 unique reflexions with $I \geq 3\sigma(I)$ were used in the refinement. The centrosymmetric space group $P\bar{1}$ was suggested by the E statistics ($\langle |E^2 - 1| \rangle = 0{\cdot}973$) and confirmed by the satisfactory refinement.



(I) R = 2-furyl

Initial attempts to solve the structure with standard direct-methods programs proved unsuccessful: therefore 'trio relations' (Table 1) each containing two negative and one positive quartet were used to construct a 20 reflexion starting set (Bonnett, Davies, Hursthouse & Sheldrick, 1978). The 4096 resulting permutations were expanded by the $\sum_2$ formula and

Table 1. *Example of a 'trio relation' of two negative and one positive quartet*

A quartet is probably negative (*i.e.* sum of phase angles = 180°) if all three cross terms, $E_{h_1+h_2}$, $E_{h_1+h_3}$, $E_{h_1+h_4}$, are small (Hauptman, 1975; Giacovazzo, 1975): one very large or two or three fairly large cross terms indicate a positive quartet. The sum of phases of the three quartets comprising the trio is identically zero, so either all three predictions are correct or two are wrong. This enhances the original probability estimates so that it is safe to assume that all three are correct.

				Cross terms				
h	*k*	*l*	*E*	*h*	*k*	*l*	*E*	
0	$\bar{5}$	$\bar{2}$	3·120	2	$\bar{7}$	$\bar{1}$	0·552	Negative quartet
2	$\bar{2}$	1	2·163	2	0	$\bar{3}$	0·061	
2	5	$\bar{1}$	2·628	$\bar{4}$	$\bar{3}$	0	0·300	
$\bar{4}$	2	2	2·120					
0	5	2	3·120	$\bar{2}$	7	1	0·552	Negative quartet
$\bar{2}$	2	$\bar{1}$	2·163	$\bar{3}$	8	$\bar{5}$	0·079	
$\bar{3}$	3	$\bar{7}$	3·191	5	$\bar{5}$	8	0·334	
5	$\overline{10}$	6	2·267					
$\bar{2}$	$\bar{5}$	1	2·628	2	$\bar{7}$	$\bar{1}$	0·552	Positive quartet
4	$\bar{2}$	$\bar{2}$	2·120	1	$\bar{8}$	8	1·866	
3	$\bar{3}$	7	3·191	$\bar{7}$	5	$\bar{5}$	1·979	
$\bar{5}$	10	$\bar{6}$	2·267					

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ranked according to the values of NQEST (DeTitta, Edmonds, Langs & Hauptman, 1975) and R_α (Roberts, Pettersen, Sheldrick, Isaacs & Kennard, 1973). The best solution on the basis of either figure of merit (NQEST −0·606 compared with −0·418 for the next, R_α 0·105 compared with 0·196) gave an E map ($E > 1{\cdot}44$) in which the highest 62 unique peaks comprised the complete structure.

The structure was refined by a blocked full-matrix least-squares method; the two independent molecules in the asymmetric unit were refined in separate blocks. A difference synthesis revealed 34/40 H atoms. H atoms bonded to C were placed in calculated positions (C—H 1·08 Å) and refined with a riding model. H(5*A*) and H(5*B*) were inserted with coordinates obtained from the difference synthesis and during refinement N—H distances were constrained to 1·00 (5) Å. A common isotropic temperature factor [0·094 (5) Å^2] was refined for all H atoms. The refinement converged at R 0·065, $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}064$, for 262 parameters; reflexions were weighted as $w = 1/\sigma^2(F_o)$.

Final atomic coordinates and isotropic temperature factors are given in Table 2 and the molecular geometry in Table 3.* Fig. 1 shows a molecule of (I*B*), with the atom numbering.

Discussion. A search of the Cambridge Crystallographic Data Centre files, accessed *via The Crystal Structure Search Retrieval Program* (Elder & Machin,

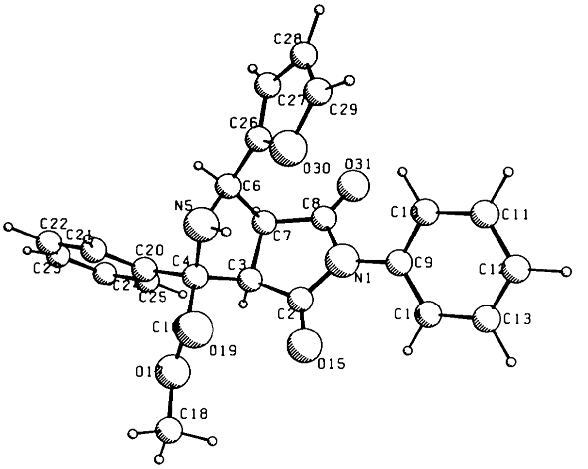

Fig. 1. Diagram of one molecule (*B*) showing atom numbering. H atoms are given the number of the C or N atom to which they are attached.

Table 2. *Fractional atomic coordinates* (×10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	*y*	*z*	*U*
Molecule *A*				
N(1)	5723 (5)	258 (4)	8823 (3)	30 (1)
C(2)	6985 (6)	676 (5)	9150 (4)	33 (2)
C(3)	6919 (6)	1545 (4)	9925 (4)	26 (2)
C(4)	7658 (6)	2522 (4)	9750 (4)	25 (2)
N(5)	6772 (5)	2775 (4)	8979 (3)	31 (1)
C(6)	5450 (6)	2697 (5)	9275 (4)	32 (2)
C(7)	5484 (6)	1770 (4)	9841 (4)	29 (2)
C(8)	4825 (6)	816 (5)	9289 (4)	35 (2)
C(9)	5412 (6)	−643 (5)	8150 (4)	33 (2)
C(10)	4276 (7)	−718 (5)	7557 (5)	46 (2)
C(11)	3987 (7)	−1603 (6)	6905 (5)	55 (2)
C(12)	4800 (7)	−2367 (6)	6833 (5)	55 (2)
C(13)	5925 (7)	−2297 (6)	7419 (5)	52 (2)
C(14)	6240 (7)	−1424 (5)	8094 (5)	43 (2)
O(15)	7953 (4)	353 (3)	8842 (3)	43 (1)
C(16)	8983 (6)	2339 (5)	9423 (5)	34 (2)
O(17)	9693 (4)	1911 (3)	10039 (3)	38 (1)
C(18)	10934 (7)	1562 (6)	9779 (5)	53 (2)
O(19)	9360 (4)	2580 (3)	8728 (3)	45 (1)
C(20)	7832 (6)	3364 (5)	10594 (4)	30 (2)
C(21)	8359 (6)	4325 (5)	10482 (5)	42 (2)
C(22)	8480 (7)	5131 (6)	11213 (5)	54 (2)
C(23)	8092 (7)	5000 (6)	12056 (5)	52 (2)
C(24)	7600 (7)	4059 (5)	12191 (5)	50 (2)
C(25)	7463 (6)	3236 (5)	11458 (4)	40 (2)
C(26)	4492 (6)	2521 (5)	8445 (4)	33 (2)
C(27)	4503 (6)	2165 (5)	7547 (4)	40 (2)
C(28)	3178 (7)	2072 (5)	7138 (5)	46 (2)
C(29)	2444 (7)	2369 (5)	7818 (5)	48 (2)
O(30)	3221 (4)	2660 (3)	8644 (3)	46 (1)
O(31)	3673 (4)	539 (3)	9256 (3)	43 (1)
Molecule *B*				
N(1)	9542 (5)	2700 (4)	4895 (4)	37 (2)
C(2)	9087 (6)	3665 (5)	5014 (5)	39 (2)
C(3)	8897 (6)	3999 (5)	6030 (4)	34 (2)
C(4)	7465 (6)	4224 (5)	6160 (4)	32 (2)
N(5)	6782 (5)	3206 (4)	6050 (4)	35 (2)
C(6)	7657 (6)	2584 (5)	6538 (4)	34 (2)
C(7)	9097 (6)	3027 (5)	6454 (4)	35 (2)
C(8)	9760 (7)	2360 (5)	5757 (5)	42 (2)
C(9)	9742 (6)	2102 (5)	4019 (4)	36 (2)
C(10)	9437 (7)	1056 (6)	3879 (5)	52 (2)
C(11)	9532 (7)	496 (6)	3001 (5)	64 (2)
C(12)	9925 (7)	979 (6)	2296 (6)	64 (2)
C(13)	10276 (7)	2011 (6)	2455 (5)	60 (2)
C(14)	10195 (7)	2585 (6)	3329 (5)	49 (2)
O(15)	8872 (4)	4170 (4)	4395 (3)	54 (1)
C(16)	6887 (6)	4791 (5)	5421 (5)	40 (2)
O(17)	7338 (4)	5769 (3)	5572 (3)	47 (1)
C(18)	6962 (7)	6375 (6)	4847 (5)	59 (2)
O(19)	6140 (4)	4419 (3)	4760 (3)	52 (1)
C(20)	7291 (6)	4789 (5)	7132 (4)	36 (2)
C(21)	6061 (7)	4767 (5)	7424 (5)	50 (2)
C(22)	5835 (7)	5256 (5)	8316 (5)	53 (2)
C(23)	6859 (7)	5773 (6)	8884 (5)	57 (2)
C(24)	8079 (7)	5808 (5)	8605 (5)	54 (2)
C(25)	8298 (7)	5315 (5)	7722 (5)	42 (2)
C(26)	7370 (6)	1489 (5)	6203 (5)	40 (2)
C(27)	7449 (7)	646 (6)	6601 (6)	63 (2)
C(28)	7035 (8)	−197 (7)	5897 (6)	76 (3)
C(29)	6740 (8)	132 (7)	5119 (7)	78 (3)
O(30)	6949 (5)	1209 (4)	5276 (4)	67 (2)
O(31)	10362 (5)	1629 (4)	5876 (3)	56 (1)

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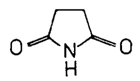
* Lists of bond angles involving the substituent groups on the diazabicyclooctane ring, hydrogen atom positions and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33994 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Molecular geometry*

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
(*a*) Bond lengths (Å)					
N(1) -C(2)	1·405 (8)	1·381 (9)	C(16)–O(17)	1·327 (8)	1·335 (8)
C(2)–C(3)	1·501 (8)	1·522 (9)	C(16)–O(19)	1·204 (9)	1·207 (8)
C(3)–C(4)	1·536 (8)	1·556 (9)	O(17)–C(18)	1·456 (8)	1·465 (9)
C(3)–C(7)	1·533 (8)	1·531 (10)	C(4)–C(20)	1·527 (8)	1·538 (9)
C(4)–N(5)	1·481 (8)	1·470 (8)	C(20)–C(21)	1·398 (9)	1·384 (10)
N(5)–C(6)	1·479 (8)	1·472 (9)	C(21)–C(22)	1·386 (9)	1·414 (10)
C(6)–C(7)	1·584 (9)	1·597 (9)	C(22)–C(23)	1·366(11)	1·370 (10)
C(7)–C(8)	1·489 (8)	1·491 (9)	C(23)–C(24)	1·372 (11)	1·366 (11)
C(8)–N(1)	1·388 (8)	1·407 (9)	C(24)–C(25)	1·402 (9)	1·403 (10)
N(1)–C(9)	1·431 (7)	1·443 (8)	C(25)–C(20)	1·388 (9)	1·376 (8)
C(9)–C(10)	1·389 (9)	1·386 (10)	C(6)–C(26)	1·479 (8)	1·466 (9)
C(10)–C(11)	1·397 (9)	1·400 (10)	C(26)–C(27)	1·331 (9)	1·341 (11)
C(11)–C(12)	1·354 (11)	1·377 (12)	C(27)–C(28)	1·439 (9)	1·420 (11)
C(12)–C(13)	1·374 (10)	1·377 (11)	C(28)–C(29)	1·335 (10)	1·299 (14)
C(13)–C(14)	1·408 (9)	1·399 (10)	C(29)–O(30)	1·382 (8)	1·415 (10)
C(14)–C(9)	1·381 (10)	1·381 (10)	O(30)–C(26)	1·393 (8)	1·377 (8)
C(2)–O(15)	1·212 (8)	1·220 (9)	C(8)–O(31)	1·225 (8)	1·209 (9)
C(4)–C(16)	1·517 (9)	1·509 (10)			
(*b*) Selected bond angles (°)					
C(2)–N(1)–C(8)	109·7 (5)	110·3 (5)	C(20)–C(4)–N(5)	113·0 (5)	108·0 (5)
C(2)–N(1)–C(9)	125·2 (5)	125·7 (6)	C(4)–N(5)–C(6)	106·2 (5)	105·6 (5)
C(8)–N(1)–C(9)	125·0 (5)	124·0 (5)	C(4)–N(5)–H(5)	112 (4)	110 (4)
N(1)–C(2)–C(3)	109·5 (5)	109·8 (6)	H(5)–N(5)–C(6)	108 (4)	113 (4)
N(1)–C(2)–O(15)	123·5 (5)	124·9 (6)	N(5)–C(6)–C(7)	103·4 (5)	106·2 (5)
O(15)–C(2)–C(3)	127·1 (5)	125·3 (6)	N(5)–C(6)–C(26)	109·2 (5)	111·7 (5)
C(2)–C(3)–C(4)	111·6 (5)	111·7 (5)	C(26)–C(6)–C(7)	113·7 (5)	116·0 (5)
C(2)–C(3)–C(7)	103·2 (4)	103·0 (5)	C(6)–C(7)–C(8)	112·0 (5)	112·4 (5)
C(7)–C(3)–C(4)	105·2 (5)	104·5 (5)	C(6)–C(7)–C(3)	103·6 (5)	103·9 (5)
C(3)–C(4)–N(5)	99·3 (4)	104·0 (5)	C(3)–C(7)–C(8)	103·7 (5)	104·6 (6)
C(3)–C(4)–C(16)	113·4 (5)	111·9 (5)	C(7)–C(8)–N(1)	109·7 (5)	108·5 (6)
C(3)–C(4)–C(20)	113·3 (5)	113·1 (5)	C(7)–C(8)–O(31)	126·2 (6)	127·6 (7)
C(16)–C(4)–N(5)	109·7 (5)	108·8 (5)	O(31)–C(8)–N(1)	124·1 (5)	123·9 (6)
C(16)–C(4)–C(20)	108·1 (5)	110·6 (5)			

1978), revealed no other structures containing a diazabicyclooctane ring system. However, the structures of syringaresinol {2,6-bis(4-hydroxy-3,5-dimethoxyphenyl)-3,7-dioxabicyclo[3.3.0]octane (Bryan & Fallon, 1976)} and dibromopinoresinol dimethyl ether {2,6-bis(2-bromo-4,5-dimethoxyphenyl)-3,7-dioxabicyclo-[3.3.0]octane (Vialard, 1968)}, both containing a dioxabicyclooctane ring system, have been reported. Unfortunately the latter is of low accuracy ($R = 0{\cdot}15$) and no attempt was made to locate the H atoms. In both syringaresinol and the present structure the H atoms at the C(3)—C(7) bridgehead are in an approximately eclipsed conformation [torsion angle H(3)—C(3)—C(7)—H(7) 19·4° (I*A*), 15·9° (I*B*), −16° syringaresinol]: the corresponding H(3)···H(7) separations are 2·54, 2·52 and 2·54 Å respectively.

The presence of the substituents O(15) and O(31) in (I) allows a π-electron delocalization and contributions from structures $O^-{-}\underset{|}{C}{=}\overset{|}{N^+}{-}\underset{|}{C}{=}O$ resulting in a planar configuration. This feature is absent from the dioxabicyclooctane ring structures but comparisons can be made with succinimide (II) (Mason, 1961) where an approximately planar structure was observed (Table 4). The present structure is less planar than succinimide; in particular the deviations of O(31), C(3) and C(7) from the least-squares plane are significantly larger. Similar averaged bond lengths are observed in the two structures, *viz.* C(sp^2)—C(sp^3) 1·501 (11) and 1·507 (9) Å; C=O 1·217 (6) and 1·227 (16) Å; C—N 1·395 (11) and 1·385 (14) Å in (I) and (II) respectively.



(II)

No significant differences in geometry are observed between the two independent molecules of (I) (Table 3) apart from two bond angles at C(4). The torsion angles defining the orientations of the substituent groups on the diazabicyclooctane ring are given in Table 5. The different orientations of the substituents at C(4) and C(6) in the two molecules, and in particular the rotation of the furyl group about C(6)—C(26), may be partially dictated by the crystal packing. No abnormally short intermolecular contacts occur.

Table 4. *Atom deviations* (Å) *from least-squares planes*

	(I*A*)	(I*B*)	(II)*
N(1)	−0·064	−0·125	0·057
O(15)	−0·026	−0·021	−0·011
O(31)	0·120	0·135	0·008
C(2)	0·016	0·009	0·017
C(3)	0·179	0·140	0·002
C(7)	−0·188	−0·163	−0·033
C(8)	−0·036	−0·017	0·003
R.m.s deviation	0·112	0·107	0·026

* The atoms of the reference structure have been renumbered to correspond to (I).

Table 5. *Torsion angles* (°)

	(I*A*)	(I*B*)
C(8)–N(1)–C(9)–C(10)	35·5	37·0
N(5)–C(4)–C(16)–O(19)	15·5	−11·1
N(5)–C(4)–C(16)–O(17)	−167·2	170·8
N(5)–C(4)–C(20)–C(21)	−61·0	−46·6
N(5)–C(6)–C(26)–C(27)	21·5	−147·6
N(5)–C(6)–C(26)–O(30)	−166·6	34·2

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The Structure of 1-Acetylprolinamide

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Abstract. $C_7H_{12}N_2O_2$, M_r = 156·19, orthorhombic, $P2_12_12_1$, a = 6·680 (9), b = 7·685 (8), c = 15·627 (14) Å, V = 802·2 (6) Å^3, Z = 4, D_m = 1·315, D_c = 1·294 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·105 mm^{-1}, F(000) = 336. 1410 observed reflections gave a final R = 0·046. Two strong intermolecular hydrogen bonds involving the H atoms of the amide group determine the crystal structure.

Introduction. Crystals of $C_7H_{12}N_2O_2$ (NACPRO) were obtained by slow evaporation of a purified specimen in acetone. They are transparent and colourless. Precise lattice parameters were obtained by least-squares fitting of the powder pattern.

For the X-ray investigation a large single crystal was ground to a sphere of 0·3 mm radius. Intensities were measured on an automatic four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation and the $\omega/2\theta$ scan mode. Two reflexions were monitored periodically during the data-collection process. Subsequent analysis of these reflexions indicated no crystal decomposition during the time required to collect the intensities. 3724 reflexions were collected in the range 1·3 < θ < 46° of which 1410 were considered as observed according to the criterion $I > 2\sigma(I)$ and used in the calculations.

The solution of this structure was quite difficult. First attempts using an older version of *MULTAN* (Main, Woolfson, Declercq & Germain, 1974) and 2000 $\sum_2$ relationships were without success. This was probably due to the weak representation of reflexions with odd k and to the small number of $\sum_2$ relationships. The structure was finally solved with a newer version of

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