Acta Cryst. (1990). C46, 829–833

Structures of Three 1-Benzazepine-2,5-diones: Cyclic Derivatives of *N*-Acyl Kynurenines

By J. M. Gulbis and M. F. Mackay

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, *Australia*

and D. E. Rivett

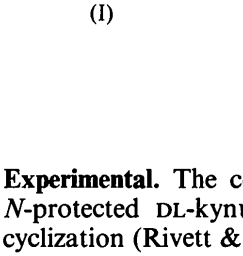
CSIRO, Division of Biotechnology, 343 *Royal Parade, Parkville, Victoria* 3052, *Australia*

(*Received* 14 *July* 1989; *accepted* 15 *August* 1989)

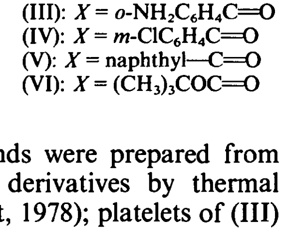
Abstract. 2-Amino-*N*-(2,3,4,5-tetrahydro-2,5-dioxo-1*H*-1-benzazepin-3-yl)benzamide (III): $C_{17}H_{15}N_3O_3$, M_r = 309·3, triclinic, $P\bar{1}$ (confirmed on refinement), a = 4·897 (2), b = 11·426 (4), c = 14·315 (7) Å, α = 76·30 (4), β = 81·99 (4), γ = 78·57 (3)°, V = 759·2 (6) Å^3, D_m(flotation) = 1·34 (1), D_x = 1·353 Mg m^{-3}, Z = 2, $F(000)$ = 318, λ(Cu $K\alpha$) = 1·5418 Å, μ = 0·65 mm^{-1}. Final R = 0·068 for 1415 observed data. 3-Chloro-*N*-(2,3,4,5-tetrahydro-2,5-dioxo-1*H*-1-benzazepin-3-yl)benzamide (IV): $C_{17}H_{13}ClN_2O_3$, M_r = 328·8, monoclinic, $P2_1/n$, a = 4·871 (1), b = 11·676 (1), c = 25·875 (4) Å, β = 90·34 (1)°, V = 1471·6 (3) Å^3, D_m(flotation) = 1·48 (1), D_x = 1·484 Mg m^{-3}, Z = 4, $F(000)$ = 680, λ(Cu $K\alpha$) = 1·5418 Å, μ = 2·33 mm^{-1}. Final R = 0·042 for 2011 observed terms. *N*-(2,3,4,5-Tetrahydro-2,5-dioxo-1*H*-1-benzazepin-3-yl)-2-naphthalenecarboxamide (V): $C_{21}H_{16}N_2O_3$, M_r = 344·4, triclinic, $P\bar{1}$ (confirmed on refinement), a = 8·216 (1), b = 8·968 (1), c = 11·381 (2) Å, α = 93·68 (1), β = 96·98 (1), γ = 97·43 (1)°, V = 822·6 (2) Å^3, D_m(flotation) = 1·39 (1), D_x = 1·386 Mg m^{-3}, Z = 2, $F(000)$ = 360, λ(Cu $K\alpha$) = 1·5418 Å, μ = 0·68 mm^{-1}. Final R = 0·051 for 1759 observed data. T = 293 (1) K in each case. The benzazepine rings are in irregular boat forms with the *N*-acyl substituents in the equatorial positions. The exocyclic NH—CO moiety adopts the usual *trans* planar conformation in all three molecules.

Introduction. Kynurenine [(I): X = H] is a major metabolic and oxidative degradation product of the amino acid tryptophan. Cyclization of *N*-acyl kynurenines (Rivett & Stewart, 1978) [(I): X = RC═O] yields 1-benzazepine-2,5-diones [(II): X = RC═O] which, because of their structural similarities to seven-membered nitrogen heterocycles exhibiting biological activity, are of considerable pharmacological interest. Of particular interest is the relationship to the biologically active 1,4-benzodiazepines which exhibit anxiolytic effects on the central nervous system (Hoffmeister & Stille, 1981). Since the discovery of a benzazepine recognition site, renewed interest has developed in these compounds derived from kynurenine as potential sources of 'natural' anxiolytic agents.

The lack of crystallographic data for the benzazepine-2,5-dione system prompted us to carry out the analyses reported herein. This work follows our X-ray study of the closely related 3*S*-3{[(1,1-dimethylethoxy)carbonyl]amino}-2,5-dioxo-2,3,4,5-tetrahydro-1*H*-1-benzazepine (VI) (Ball, Wong, Capuano, Gulbis, Mackay & Alewood, 1990).



(I)



(II): X = RC═O
(III): X = o-$NH_2C_6H_4$C═O
(IV): X = m-ClC_6H_4C═O
(V): X = naphthyl—C═O
(VI): X = $(CH_3)_3$COC═O

Experimental. The compounds were prepared from *N*-protected DL-kynurenine derivatives by thermal cyclization (Rivett & Stewart, 1978); platelets of (III) from aqueous ethanol, prismatic crystals of (IV) from dimethylformamide and needles of (V) from a dimethylformamide–ethanol mixture; crystals *ca* 0·58 × 0·11 × 0·03 (III), 0·39 × 0·21 × 0·17 (IV) and 0·42 × 0·09 × 0·05 mm (V) aligned on a Rigaku-AFC diffractometer; cell parameters determined by least squares from 2θ values for 25 strong reflections (34 < 2θ < 75°) (III), (41 < 2θ < 83°) (IV) and (41 < 2θ < 75°) (V); Cu $K\alpha$ radiation (graphite-crystal monochromator); ω–2θ scan, 2θ scan rate 2° min^{-1}, scan

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range ($\Delta\omega$) $(1·2 + 0·5 \tan\theta)^\circ$, $2\theta_{\max} = 130^\circ$, 10 s stationary background counts; three standard reflections monitored every 50 reflections, no significant intensity variation; 2545 non-equivalent terms for (III), h −5 to 5, k −13 to 13, l 0 to 16; 2565 non-equivalent terms for (IV), h −5 to 5, k 0 to 13, l 0 to 30; 2604 non-equivalent terms for (V), h −9 to 9, k −10 to 10, l 0 to 13; intensities corrected for Lorentz and polarization effects and for absorption, transmission factors 0·913 to 0·979 (III), 0·672 to 0·784 (IV) and 0·871 to 0·966 (V); for (IV) isotropic extinction correction of form $F = F_c[1 - (2·26 \times 10^{-6}F^2/\sin\theta)]$ applied to calculated structure amplitudes; six low-angle terms (100, $\bar{1}10$, $\bar{1}20$, $1\bar{1}1$, 101, $\bar{1}21$,) and two low-angle terms ($0\bar{2}2$, $1\bar{2}2$) apparently seriously affected by extinction omitted from the final refinements of (III) and (V) respectively. Structures solved by direct methods with *SHELXS*86 (Sheldrick, 1985) and refined with *SHELX*76 (Sheldrick, 1976). For (IV) and (V) H-atom sites located on difference maps and H coordinates refined with isotropic temperature factors; for (III) H atoms included at idealized positions (C—H 1·08 and N—H 0·97 Å) and given an overall isotropic temperature factor [$B = 7·0\,(4)$ Å^2]. Refinement with anisotropic temperature factors assigned to the C,N,O,Cl atoms with terms for which $I > \sigma(I)$; at convergence $R = 0·068$, $wR = 0·082$, $S = 1·06$ (218 parameters varied) for (III); $R = 0·042$, $wR = 0·053$, $S = 1·38$ (260 parameters varied) for (IV); $R = 0·051$, $wR = 0·052$, $S = 1·19$ (296 parameters varied) for (V); function minimized $\sum w(|\Delta F|)^2$ with $w = [\sigma^2(|F|) + m|F|^2]^{-1}$ for which $m = 0·003$ (III), 0·0009 (IV) and 0·0008 (V); $(\Delta/\sigma)_{\max} = 0·02$ (III), 0·004 (IV) and 0·005 (V); $(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min} = +0·24$, $-0·25$ (III), $+0·21$, $-0·26$ (IV) and $+0·25$, $-0·23$ e Å^{-3} (V). Atomic scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Figures were prepared from the output of *ORTEP*II (Johnson, 1976). Calculations performed on a VAX11/780 computer.

Discussion. Final atomic coordinates of the non-H atoms for structures (III), (IV) and (V) are given in Table 1.* The molecular conformations for the three structures are illustrated in Fig. 1, which also includes the atom numbering. Bond lengths and angles are given in Table 2 and hydrogen-bond geometry in Table 4.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors for the non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
(*a*) $C_{17}H_{15}N_3O_3$ (III)				
N(1)	−8204 (9)	1253 (4)	−747 (3)	4·6 (1)
C(2)	−8377 (11)	576 (4)	−1388 (4)	4·3 (1)
O(2)	−9665 (9)	−287 (3)	−1156 (3)	6·7 (1)
C(3)	−7008 (10)	946 (4)	−2390 (3)	3·7 (1)
C(4)	−8480 (11)	2193 (4)	−2871 (4)	4·3 (1)
C(5)	−7747 (11)	3263 (4)	−2579 (4)	4·6 (1)
O(5)	−8279 (9)	4267 (3)	−3098 (3)	6·8 (1)
C(5*a*)	−6387 (10)	3122 (4)	−1680 (4)	4·2 (1)
C(6)	−4875 (12)	4026 (5)	−1657 (5)	5·6 (1)
C(7)	−3666 (13)	4047 (6)	−849 (6)	7·7 (2)
C(8)	−4078 (13)	3167 (6)	−17 (6)	7·7 (2)
C(9)	−5560 (12)	2252 (5)	−17 (4)	5·9 (1)
C(9*a*)	−6667 (11)	2206 (4)	−834 (4)	4·3 (1)
N(10)	−7035 (8)	30 (3)	−2939 (3)	3·8 (1)
C(11)	−4688 (10)	−700 (4)	−3180 (3)	3·4 (1)
O(11)	−2429 (6)	−623 (3)	−2944 (3)	6·0 (1)
C(12)	−4983 (9)	−1604 (4)	−3741 (3)	3·4 (1)
C(13)	−6866 (11)	−1267 (4)	−4450 (4)	4·3 (1)
C(14)	−7164 (12)	−2065 (5)	−4999 (4)	5·5 (1)
C(15)	−5590 (13)	−3227 (5)	−4835 (4)	5·7 (1)
C(16)	−3703 (13)	−3571 (4)	−4155 (4)	5·2 (1)
C(17)	−3339 (10)	−2778 (4)	−3600 (4)	4·1 (1)
N(17)	−1507 (10)	−3162 (4)	−2885 (4)	5·5 (1)
(*b*) $C_{17}H_{13}ClN_2O_3$ (IV)				
Cl	1339 (1)	7192 (1)	7551 (0)	4·79 (2)
N(1)	2490 (4)	11418 (2)	10009 (1)	2·87 (4)
C(2)	3112 (4)	10793 (2)	9586 (1)	2·52 (4)
O(2)	1882 (4)	9894 (1)	9498 (1)	3·50 (3)
C(3)	5253 (4)	11232 (2)	9215 (1)	2·44 (4)
C(4)	5008 (5)	12535 (2)	9131 (1)	3·02 (4)
C(5)	6591 (5)	13177 (2)	9535 (1)	3·29 (4)
O(5)	8555 (4)	13769 (2)	9407 (1)	5·36 (4)
C(5*a*)	5779 (5)	13086 (2)	10083 (1)	3·01 (4)
C(6)	6952 (6)	13880 (3)	10426 (1)	4·17 (6)
C(7)	6221 (6)	13944 (3)	10936 (1)	4·90 (6)
C(8)	4233 (6)	13201 (3)	11120 (1)	4·81 (6)
C(9)	3074 (6)	12399 (2)	10801 (1)	3·82 (5)
C(9*a*)	3823 (5)	12315 (2)	10281 (1)	2·80 (4)
N(10)	4936 (4)	10609 (2)	8736 (1)	2·81 (4)
C(11)	6995 (4)	10450 (2)	8405 (1)	2·42 (4)
O(11)	9304 (3)	10846 (2)	8482 (1)	3·42 (3)
C(12)	6324 (4)	9763 (2)	7935 (1)	2·41 (4)
C(13)	4312 (5)	8918 (2)	7952 (1)	2·74 (4)
C(14)	3723 (5)	8293 (2)	7512 (1)	3·20 (4)
C(15)	5021 (6)	8516 (2)	7052 (1)	3·79 (5)
C(16)	6991 (6)	9368 (3)	7036 (1)	3·90 (5)
C(17)	7679 (5)	9971 (2)	7477 (1)	3·09 (4)
(*c*) $C_{21}H_{16}N_2O_3$ (V)				
N(1)	−1347 (3)	−6528 (3)	−1152 (2)	2·86 (5)
C(2)	−2327 (3)	−5850 (3)	−477 (3)	2·49 (6)
O(2)	−2441 (2)	−4503 (2)	−485 (2)	3·18 (4)
C(3)	−3350 (4)	−6900 (3)	245 (3)	2·49 (5)
C(4)	−4756 (4)	−7825 (4)	−596 (3)	2·80 (6)
C(5)	−4277 (4)	−9107 (4)	−1324 (3)	3·04 (6)
C(5*a*)	−2508 (4)	−9265 (3)	−1428 (3)	2·64 (6)
O(5)	−5358 (3)	−10102 (3)	−1773 (3)	5·86 (6)
C(6)	−2181 (4)	−10736 (4)	−1679 (3)	3·56 (7)
C(7)	−621 (4)	−11058 (4)	−1796 (3)	4·05 (7)
C(8)	679 (4)	−9882 (4)	−1674 (3)	3·95 (7)
C(9)	398 (4)	−8417 (4)	−1427 (3)	3·36 (7)
C(9*a*)	−1189 (4)	−8083 (3)	−1309 (3)	2·55 (6)
N(10)	−3994 (3)	−6054 (3)	1163 (2)	2·81 (5)
C(11)	−2951 (4)	−5311 (3)	2085 (3)	2·79 (6)
O(11)	−1442 (3)	−5352 (2)	2159 (2)	3·53 (4)
C(12)	−3690 (4)	−4413 (3)	2976 (3)	2·76 (6)
C(13)	−5320 (4)	−4711 (4)	3157 (3)	2·96 (6)
C(14)	−5979 (4)	−3814 (4)	4001 (3)	3·03 (6)
C(15)	−7665 (4)	−4094 (4)	4186 (3)	3·93 (7)
C(16)	−8248 (5)	−3227 (5)	5027 (3)	4·86 (9)
C(17)	−7214 (5)	−2055 (5)	5703 (4)	5·07 (9)
C(18)	−5598 (6)	−1742 (4)	5542 (3)	4·56 (8)
C(19)	−4940 (4)	−2607 (3)	4677 (3)	3·36 (7)
C(20)	−3252 (5)	−2338 (4)	4478 (3)	3·93 (7)
C(21)	−2654 (4)	−3208 (4)	3666 (3)	3·50 (7)

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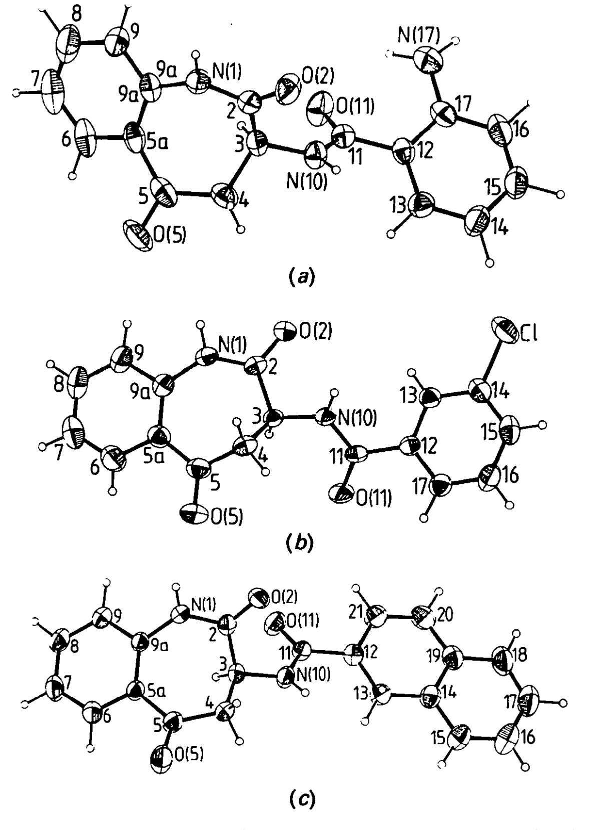
* Lists of anisotropic thermal parameters, H-atom parameters, short intermolecular contact distances and lists of structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52516 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	(III)	(IV)	(V)
N(1)—C(2)	1·353 (8)	1·351 (4)	1·351 (4)
N(1)—C(9*a*)	1·415 (7)	1·417 (3)	1·419 (4)
C(2)—O(2)	1·230 (7)	1·229 (3)	1·224 (3)
C(2)—C(3)	1·498 (7)	1·511 (3)	1·527 (4)
C(3)—C(4)	1·513 (6)	1·541 (3)	1·523 (4)
C(3)—N(10)	1·453 (7)	1·445 (4)	1·443 (4)
C(4)—C(5)	1·502 (8)	1·497 (4)	1·496 (5)
C(5)—C(5*a*)	1·491 (8)	1·478 (4)	1·496 (5)
C(5)—O(5)	1·211 (5)	1·227 (3)	1·213 (4)
C(5*a*)—C(6)	1·394 (9)	1·403 (4)	1·399 (5)
C(5*a*)—C(9*a*)	1·411 (7)	1·409 (3)	1·402 (4)
C(6)—C(7)	1·378 (12)	1·371 (4)	1·370 (5)
C(7)—C(8)	1·384 (10)	1·387 (5)	1·388 (5)
C(8)—C(9)	1·386 (10)	1·368 (4)	1·380 (5)
C(9)—C(9*a*)	1·372 (9)	1·400 (4)	1·395 (5)
N(10)—C(11)	1·335 (6)	1·336 (3)	1·350 (4)
C(11)—O(11)	1·226 (7)	1·231 (3)	1·238 (4)
C(11)—C(12)	1·489 (7)	1·491 (4)	1·489 (5)
C(12)—C(13)	1·401 (7)	1·392 (3)	1·374 (5)
C(12)—C(17)	1·406 (6)	1·381 (4)	
C(12)—C(21)			1·414 (4)
C(13)—C(14)	1·376 (9)	1·381 (4)	1·415 (5)
C(14)—C(15)	1·382 (7)	1·376 (4)	1·419 (5)
C(14)—C(19)			1·410 (4)
C(14)—Cl		1·736 (3)	
C(15)—C(16)	1·372 (9)	1·383 (4)	1·365 (5)
C(16)—C(17)	1·389 (8)	1·380 (4)	1·387 (5)
C(17)—N(17)	1·390 (8)		
C(17)—C(18)			1·358 (6)
C(18)—C(19)			1·415 (5)
C(19)—C(20)			1·425 (5)
C(20)—C(21)			1·349 (5)
C(2)—N(1)—C(9*a*)	130·1 (4)	134·2 (3)	128·7 (2)
N(1)—C(2)—O(2)	120·9 (4)	120·0 (2)	122·3 (2)
N(1)—C(2)—C(3)	117·1 (4)	119·4 (2)	115·2 (2)
O(2)—C(2)—C(3)	121·9 (4)	120·6 (2)	122·4 (2)
C(2)—C(3)—C(4)	109·7 (4)	111·8 (2)	108·5 (2)
C(2)—C(3)—N(10)	109·9 (3)	107·7 (2)	111·0 (2)
C(4)—C(3)—N(10)	111·6 (3)	111·6 (2)	110·6 (2)
C(3)—C(4)—C(5)	115·7 (4)	110·9 (2)	115·4 (2)
C(4)—C(5)—C(5*a*)	122·1 (4)	119·6 (3)	122·2 (3)
C(4)—C(5)—O(5)	118·3 (4)	119·5 (3)	118·4 (2)
C(5*a*)—C(5)—O(5)	119·6 (4)	120·8 (3)	119·2 (2)
C(5)—C(5*a*)—C(6)	116·6 (4)	116·7 (3)	115·6 (2)
C(5)—C(5*a*)—C(9*a*)	125·6 (4)	125·4 (3)	125·9 (2)
C(6)—C(5*a*)—C(9*a*)	117·6 (4)	117·8 (3)	118·4 (2)
C(5*a*)—C(6)—C(7)	122·5 (5)	122·5 (3)	122·3 (3)
C(6)—C(7)—C(8)	118·6 (6)	118·8 (3)	118·9 (3)
C(7)—C(8)—C(9)	120·3 (5)	120·5 (3)	120·2 (3)
C(8)—C(9)—C(9*a*)	120·9 (5)	121·3 (3)	121·1 (3)
N(1)—C(9*a*)—C(5*a*)	123·7 (4)	126·9 (3)	124·9 (3)
N(1)—C(9*a*)—C(9)	116·2 (5)	114·1 (3)	115·9 (3)
C(5*a*)—C(9*a*)—C(9)	120·0 (4)	119·0 (3)	119·0 (2)
C(3)—N(10)—C(11)	121·3 (3)	122·9 (2)	119·9 (2)
N(10)—C(11)—O(11)	121·1 (3)	122·2 (2)	120·8 (2)
N(10)—C(11)—C(12)	116·4 (3)	115·8 (2)	117·2 (2)
O(11)—C(11)—C(12)	122·5 (3)	122·0 (2)	122·0 (2)
C(11)—C(12)—C(13)	119·5 (4)	120·4 (2)	122·9 (2)
C(11)—C(12)—C(17)	121·4 (4)	120·1 (2)	
C(11)—C(12)—C(21)			118·0 (2)
C(13)—C(12)—C(17)	119·0 (4)	119·5 (2)	
C(13)—C(12)—C(21)			119·1 (2)
C(12)—C(13)—C(14)	121·4 (4)	119·4 (2)	121·1 (3)
C(13)—C(14)—C(19)			119·4 (3)
C(15)—C(14)—C(19)			118·9 (3)
C(13)—C(14)—C(15)	118·9 (5)	121·3 (2)	121·8 (3)
C(13)—C(14)—Cl		118·6 (2)	
C(15)—C(14)—Cl		120·1 (2)	
C(14)—C(15)—C(16)	120·7 (5)	119·0 (2)	120·1 (3)
C(15)—C(16)—C(17)	121·5 (4)	120·5 (2)	120·8 (3)
C(12)—C(17)—C(16)	118·4 (4)	120·3 (2)	
C(12)—C(17)—N(17)	120·9 (4)		
C(16)—C(17)—N(17)	120·6 (4)		
C(16)—C(17)—C(18)			120·8 (3)
C(17)—C(18)—C(19)			120·4 (3)
C(14)—C(19)—C(18)			119·0 (3)
C(14)—C(19)—C(20)			118·2 (3)
C(18)—C(19)—C(20)			122·8 (3)
C(19)—C(20)—C(21)			121·3 (3)
C(12)—C(21)—C(20)			120·9 (3)

As observed in crystals of (VI) which contain two independent molecules (Ball *et al.*, 1990), the benzazepine rings are in an irregular boat conformation (see Table 3*a*). The *N*-acyl substituents at C(3) occupy the equatorial positions with the peptide bonds adopting the usual *trans*-planar conformation. In each structure the five atoms, C(3), N(10), C(11), O(11), C(12) are coplanar to within experimental error [*cf.* ± 0·05 (1) Å in (VI)] and the interplanar angles given in Table 3(*b*) define the gross shapes of the molecules. In (III) the peptide group is twisted by only 10° from coplanarity with the H(3)—C(3) bond so that a short H(3)···O(11) spacing of 2·27 Å results. In (IV) and (V) the relative orientations of the group to the adjacent C—H bond, reflected in the torsion angles H(3)—C(3)—N(10)—C(11) of −37 (2) and +50 (2)° respectively [*cf.* −6 and −24° in (VI)] are such that a much greater rotation about the C(3)—N(10) bond has occurred than is observed in (III). The different conformations adopted by the three molecules are most likely a consequence of the differing hydrogen bonding schemes (Table 4) and crystal packing modes in the three structures (Fig. 2).



(*a*)

(*b*)

(*c*)

Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 50% probability. The C symbol is omitted and H atoms are denoted by spheres of arbitrary radius. (*a*) $C_{17}H_{15}N_3O_3$ (III), (*b*) $C_{17}H_{13}ClN_2O_3$ (IV), (*c*) $C_{21}H_{16}N_2O_3$ (V).

Table 3. *Selected torsion and interplanar angles* (°)

Values for the two independent molecules of (VI) (Ball *et al.*, 1990) are included for comparison.

	(III)	(IV)	(V)	(VI)	
(*a*) Torsion angles					
N(1)—C(2)—C(3)—C(4)	−65·2 (6)	−40·2 (3)	−73·9 (3)	−56·7 (3)	−67·9 (3)
C(2)—C(3)—C(4)—C(5)	78·4 (5)	86·6 (2)	77·3 (3)	86·1 (3)	73·6 (3)
C(3)—C(4)—C(5)—C(5*a*)	−18·0 (7)	−63·6 (3)	−13·2 (5)	−37·9 (4)	−8·9 (4)
C(4)—C(5)—C(5*a*)—C(9*a*)	−28·3 (8)	9·1 (4)	−26·8 (5)	−12·3 (5)	−32·4 (4)
C(5)—C(5*a*)—C(9*a*)—N(1)	3·1 (8)	6·9 (4)	−4·7 (5)	0·3 (5)	−0·9 (4)
C(5*a*)—C(9*a*)—N(1)—C(2)	40·4 (8)	24·2 (5)	40·5 (5)	41·4 (4)	43·6 (4)
C(9*a*)—N(1)—C(2)—C(3)	−7·4 (8)	−18·5 (4)	2·5 (4)	−14·6 (4)	−4·3 (4)
C(9*a*)—N(1)—C(2)—O(2)	174·3 (5)	163·7 (3)	−174·4 (3)	167·1 (3)	178·2 (2)
O(5)—C(5)—C(5*a*)—C(6)	−23·3 (8)	13·1 (4)	−20·7 (5)	−8·1 (5)	−25·0 (4)
O(2)—C(2)—C(3)—N(10)	−9·9 (7)	14·7 (3)	−18·7 (4)	−1·6 (4)	−13·5 (3)
C(2)—C(3)—N(10)—C(11)	−109·3 (5)	−154·0 (2)	−67·9 (4)	127·0 (3)	−144·5 (2)
C(3)—N(10)—C(11)—C(12)*	179·9 (4)	178·6 (2)	177·7 (3)	176·0 (3)	174·7 (2)
C(3)—N(10)—C(11)—O(11)	0·1 (7)	−1·5 (4)	−0·4 (4)	−4·0 (4)	−7·1 (4)
C(4)—C(3)—N(10)—C(11)	128·8 (5)	83·0 (3)	171·6 (3)	112·1 (3)	93·7 (3)
N(1)—C(2)—C(3)—N(10)	171·8 (4)	−163·1 (2)	164·4 (2)	−179·8 (2)	169·1 (2)
N(10)—C(11)—C(12)—C(13)	38·1 (6)	−29·7 (3)	24·0 (5)		

(*b*) Interplanar angles

Plane 1: C(5*a*), C(6), C(7), C(8), C(9), C(9*a*)
Plane 2: C(3), N(10), C(11), O(11), C(12)
Plane 3: C(12), C(13), C(14), C(15), C(16), C(17)

Planes	(III)	(IV)	(V)	(VI)	
1,2	92·9	148·1	131·7	107·6	67·9
2,3	143·0	149·6	156·9		
1,3	55·2	1·8	34·8†		

* Replace C(12) with O(12) for (VI).

† Plane 3 in (V) also contains atoms C(18), C(19), C(20), C(21).

Table 4. *Hydrogen-bonding distances* (Å) *and angles* (°) *in* (III), (IV) *and* (V)

X—H···*Y*	*X*···*Y*	H···*Y*	*X*—H	*X*—H···*Y*
(III)				
N(1)—H(N1)···O(2)^{i}	2·823 (6)	1·86 (3)	0·97	172 (3)
N(10)—H(N10)···O(11)^{ii}	2·885 (6)	1·92 (4)	0·97	172 (3)
N(17)—H(17*b*)···O(5)^{iii}	3·110 (6)	2·18 (4)	0·97	160 (3)
N(17)—H(17*a*)···O(11)*	2·829 (3)	2·16	0·97	128
(IV)				
N(1)—H(N1)···O(2)^{iv}	2·923 (3)	2·09 (3)	0·85 (3)	168 (2)
N(10)—H(N10)···O(11)^{v}	2·831 (3)	2·07 (3)	0·82 (4)	155 (3)
(V)				
N(1)—H(N1)···O(11)^{vi}	3·049 (3)	2·16 (3)	0·91 (3)	167 (1)
N(10)—H(N10)···O(2)^{vii}	3·050 (3)	2·19 (3)	0·87 (3)	173 (2)

Transformations of the coordinates (x,y,z) are denoted by superscripts: (i) $2-x, -y, -z$; (ii) $1+x, y, z$; (iii) $-1+x, 1+y, z$; (iv) $-x, 2-y, 2-z$; (v) $-1+x, y, z$; (vi) $-x, 1-y, -z$; (vii) $1-x, 1-y, -z$.

* Intramolecular interaction.

Unlike the structure of (VI) in which the peptide nitrogen, N(10), forms an intramolecular hydrogen bond with the exocyclic oxygen, O(2), of the benzazepinedione system, the peptide N—H bonds in (III)–(V) are directed away from O(2). It is only in (III) in which an intramolecular H-bonding interaction is observed. This is between the exocyclic nitrogen, N(17), and the peptide oxygen, O(11), the N(17)···O(11) and H(17*a*)···O(11) distances being 2·829 (3) and 2·16 Å respectively with the N—H···O angle 128°.

The bond lengths and angles (Table 2*a*,*b*) are in good agreement in the three structures and similar to values found in other related ones. A shortening of the C(9*a*)—N(1) bond length [values range from 1·410 (5) to 1·416 (3) Å] from the C(sp^2)—N(sp^2) single bond length of 1·470 (5) Å proposed by Camerman (1970) is indicative of some electron delocalization between the amide group and its associated aromatic ring. This is accompanied by a slight lengthening of the C(2)—O(2) carbonyl bonds to a mean length of 1·229 (4) Å. There is no significant shortening of the C(5*a*)—C(5) bonds but the associated carbonyl bonds are twisted from their respective ring planes by varying amounts [see torsion angles O(5)—C(5)—C(5*a*)—C(6)]. Similar features are observed in (VI).

The crystal packings are illustrated in Fig. 2. Apart from H(17*a*) in (III) which forms an intramolecular hydrogen bond (see earlier) all the nitrogen protons are involved in intermolecular hydrogen bonding (Table 3). In (III) and (IV) the molecules are linked into dimers by interactions between N(1) and O(2) of the benzazepinedione system of adjacent molecules related by an inversion centre. The dimers are linked into layers along the [100] and [010] directions in (III) and into columns extending along [100] in (IV). In the latter, each alternate column contains dimers of a similar orientation. In the struc-

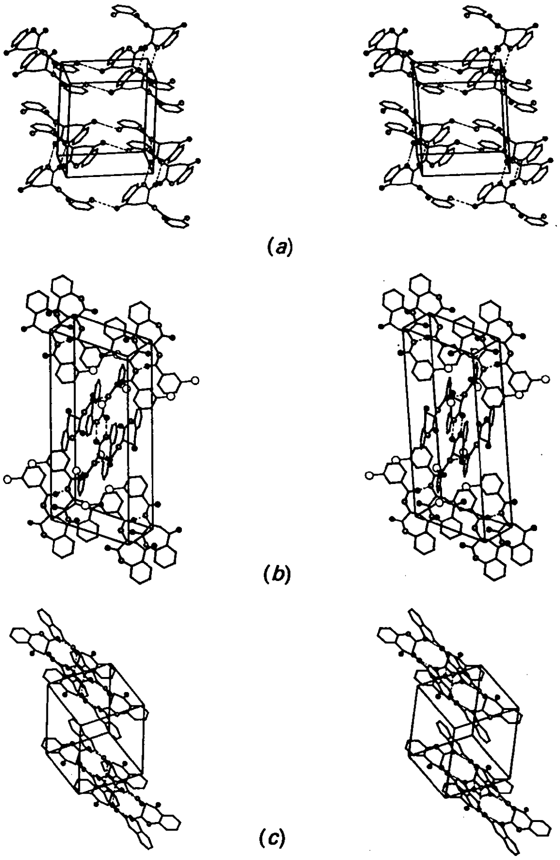


Fig. 2. Stereoviews of the crystal packings. Direction of projections *a*, the *c* axes are vertical. (*a*) $C_{17}H_{15}N_3O_3$ (III), (*b*) $C_{17}H_{13}ClN_2O_3$ (IV), (*c*) $C_{21}H_{16}N_2O_3$ (V).

ture of (V) each molecule is linked to two adjacent molecules across inversion centres. These interactions result in molecular layers extending along the [100] and [010] directions. The naphthyl rings are oriented with a significant overlap of their π-electron systems (the spacing between the rings is 3·47 Å), and form layers of hydrophobic regions sandwiched between layers of hydrophilic regions in the crystal.

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Structure of 7-Dimethylamino-4-trifluoromethylcoumarin

By K. Chinnakali, K. Sivakumar and S. Natarajan

Department of Physics, Anna University, Madras 600 025, India

(*Received* 26 *May* 1989; *accepted* 15 *August* 1989)

Abstract. $C_{12}H_{10}F_3NO_2$, $M_r = 257·2$, orthorhombic, *Pnma*, $a = 15·161$ (2), $b = 6·880$ (2), $c = 10·719$ (1) Å, $V = 1118·1$ (4) Å^3, $Z = 4$, $D_m = 1·537$, $D_x = 1·528$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·5418$ Å, $\mu = 11·727$ cm^{-1}, $F(000) = 528$, $T = 298$ K, final R value is 0·050 for 847 observed reflections. The molecule lies on the mirror plane with two of the F atoms related by mirror symmetry. In the mirror plane the molecules are linked by hydrogen bonds of the C—H···O type with C···O = 3·319 (4) Å, C—H···O = 164 (4)°.

Introduction. Aminocoumarins, which are used as laser dyes for the blue-green spectral region (Drexhage, 1973), vary in their photophysical properties for different kinds of chemical substitutions (Jones, Jackson & Kanoktanaporn, 1980; Jones, Jackson, Choi & Bergmark, 1985; Masilamani, Sastikumar, Natarajan & Natarajan, 1987). The title compound (Fig. 1), a fluorinated aminocoumarin also called coumarin 485, is found to give low fluorescence quantum yield in polar solvents and enhanced performance in low polarity solvents, unlike its unfluorinated analogue (Schimitschek, Trias, Hammond & Atkins, 1974; Guo & Feng, 1987). The structural study of this compound may be useful in understanding the effect of the trifluoromethyl group in the excited state dynamics of the molecule.

Experimental. The compound was from Exciton (USA); greenish yellow needle shaped crystals were from a mixture of aqueous ethanol and chloroform, D_m by flotation method, crystal size 0·5 × 0·3 × 0·1 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Cell parameters were from least-squares fit of 25 reflections in the range $30 < \theta < 45°$; $\omega/2\theta$ scan technique; intensity variation of two standard reflections monitored for crystal stability and orientation at every 100 reflections was less than 3%. 1101 unique reflections were measured with $\theta \leq 70°$; 847 were judged observed with $|F_o| > 4\sigma(|F_o|)$. $h = 0$ to 18, $k = 0$ to 8 and $l = 0$ to 13; intensity data were corrected for Lp but not for absorption. From the systematic

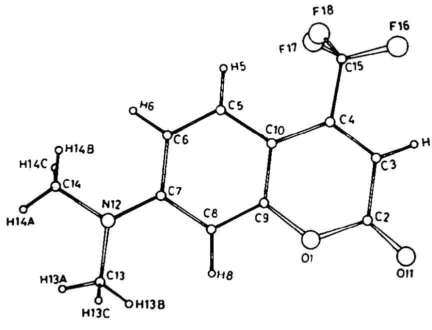

Fig. 1. Numbering scheme for the molecule.

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