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The Crystal and Molecular Structure of BNA, a Cyclotetracondensate from Quaternary Salts of Nicotinamide

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Four molecules of quaternary salts of nicotinamide cyclocondense to form a new product (BNA). The crystals of the title compound ($C_{52}H_{48}N_8O_4$) are monoclinic, space group $P2_1/c$, with $Z = 4$, $a = 14{\cdot}357$ (3), $b = 10{\cdot}736$ (1), $c = 34{\cdot}017$ (6) Å and $\beta = 123{\cdot}38$ (3)°. The structure has been determined by direct and Fourier methods and refined by least-squares analysis to an R value of 0·067 for 2472 observed reflexions. Four intramolecular hydrogen bonds involving the O atoms may explain the lipophilic properties of the molecule.

Introduction

A new reaction of quaternary salts of nicotinamide has been found and checked with more than 20 salts, differently substituted at the pyridinium N (Gündel, 1973; Gündel, Buecher & Hagedorn, 1974): four molecules of nicotinamide salts cyclize on addition of the equivalent amount of base. The cyclotetracondensate BNA, the formula of which is given in Fig. 1, results after elimination of hydrogen chloride from 1-benzyl-3-carbamoylpyridinium chloride.

The cyclocondensed products are lipophilic and can be split quantitatively by acids, such as hydrogen chloride, to the quaternary salts of nicotinamide. The possibility of transforming the hydrophilic salts of nicotinamide to a lipophilic form is of great interest.

As nicotinamide is part of the coenzyme NAD (nicotinamide adenine dinucleotide) it is suggested that NAD can cyclize in organisms in the same way.

To confirm the structure and conformation of the new cyclotetracondensate, BNA was submitted to an X-ray structure analysis.

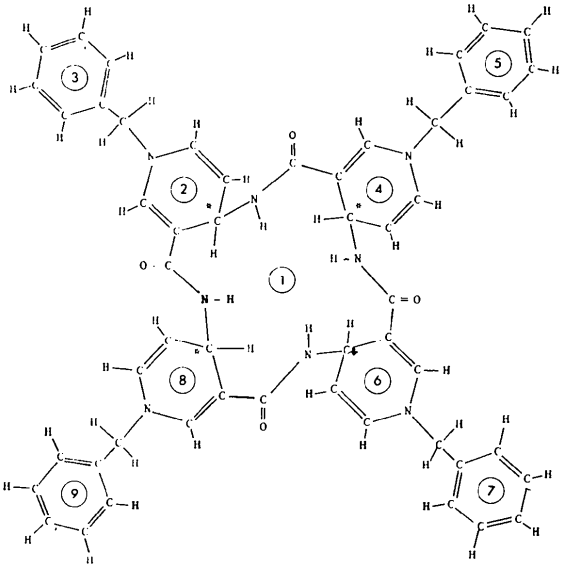

Fig. 1. BNA: planar representation.

Experimental

BNA was crystallized from a mixture of CH_2Cl_2 and CH_3CN as transparent, light-yellow prismatic single crystals elongated along the *c* axis. Precise lattice parameters were obtained by least-squares fitting of the θ values for 24 reflexions measured on a four-circle diffractometer. Table 1 shows the crystallographic data.

X-ray intensities were measured on an automatic Philips PW 1100 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation and pulse-height discrimination. A single crystal with dimensions 0·2 × 0·2 × 0·5 mm was used for collecting the intensities of 7339 independent reflexions ($2° < \theta < 25°$) in the $\omega/2\theta$ scan mode. Of these, 2472 were considered as 'observed' according to the criterion $I > 2\sigma(I)$ and used for the refinement step. Two reflexions were monitored periodically during the data-collection process and showed no crystal decomposition. No correction was made for absorption.

Table 1. *Crystal data for BNA*

Standard deviations, given in parentheses, refer to the least significant digits.

$C_{52}H_{48}N_8O_4$

M_r	849·01	V	4378 (3) Å^3
λ (Mo $K\alpha$)	0·7107 Å	Z	4
a	14·357 (3)	D_c	1·288 g cm
b	10·736 (1)	μ(Mo $K\alpha$)	0·90 cm^{-1}
c	34·017 (6)	F(000)	1792
β	123·38 (3)°	Space group	$P2_1/c$

Determination of the structure

Phases of the 300 largest normalized structure factors were calculated by the multisolution tangent formula with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The best phased E map revealed ~80% of the non-hydrogen atoms, mainly from the central part of the compound, but showed the orientation of all the rings in the molecule. Successive Fourier syntheses gave the positions of the remaining non-hydrogen atoms of the molecule, confirming the arrangement of all the rings. Structure factors calculated with these coordinates and an assumed overall temperature factor of 3·17 Å^2 gave a discrepancy index $R = 0·26$. Scattering factors for neutral C, N, O were taken from Cromer & Mann (1967), those for H atoms from *International Tables for X-ray Crystallography* (1962).

After four cycles of full-matrix isotropic refinement for the 2472 observed reflexions and two more cycles with anisotropic temperature factors (blocked refinement), the conventional R index was 0·133. A difference synthesis calculated with those observed reflexions with $\sin\theta/\lambda < 0·5$ showed ~80% of the H atoms with electron densities ranging from 0·6 to 0·3 e Å^{-3}. The remaining H atoms appeared as rather broad maxima in the synthesis.

An appropriate weighting scheme for the refinement was $w = w_1w_2$ where $w_1 = 1/\sigma_1^2$ and $w_2 = 1/\sigma_2^2$ with $\sigma_1 = a + b|F_o|$ and $\sigma_2^2 = c + d\sin\theta/\lambda$ (coefficients given in Table 2), calculated by the program *PESOS* (Martínez-Ripoll & Cano, 1975). All the H atoms were placed at the expected positions with the program *HSEARCH* (Fayos & Martínez-Ripoll, 1975). After six cycles of blocked least-squares refinement assuming isotropic temperature factors for the H atoms, the final unweighted and weighted disagreement indices were $R = 0·067$ and $R = 0·057$, where $R_w = (\Sigma\, w\Delta^2/\Sigma\, w|F_o|^2)^{1/2}$. A final difference syn-

Table 2. *Coefficients for the weighting scheme*

	a	b		c	d
$0 \le F_o < 2·85$	7·06	−1·28	$0 \le \sin\theta/\lambda < 0·340$	0·96	−0·66
$2·85 \le F_o < 12·00$	2·48	0·24	$0·340 \le \sin\theta/\lambda < 0·425$	−0·98	4·84
$12·00 \le F_o < 20·00$	9·02	−0·32	$0·425 \le \sin\theta/\lambda < 0·500$	2·31	−2·72
$20·00 \le F_o \le 300·00$	2·64	0·00	$0·500 \le \sin\theta/\lambda \le 0·600$	−1·30	4·48

Table 3. *Atomic parameters*

Anisotropic thermal parameters have been multiplied by 10^3 and isotropic parameters by 10^4. Standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(11)	0·0055 (6)	0·9404 (6)	0·1139 (2)	54 (5)	30 (4)	39 (5)	4 (4)	21 (4)	−5 (3)
C(12)	−0·0892 (6)	1·0045 (7)	0·2281 (2)	89 (6)	59 (5)	61 (5)	13 (4)	56 (5)	−5 (4)
C(13)	0·1706 (6)	0·6522 (7)	0·1612 (2)	46 (4)	50 (5)	35 (4)	8 (4)	20 (4)	7 (4)
C(14)	0·2595 (6)	0·2969 (6)	0·1024 (2)	80 (5)	48 (5)	75 (5)	4 (4)	53 (5)	−13 (4)
C(15)	−0·1256 (5)	0·5922 (7)	0·1178 (2)	48 (5)	52 (5)	53 (5)	0 (4)	31 (4)	0 (4)
C(16)	−0·4171 (6)	0·8854 (8)	0·0850 (3)	68 (5)	86 (6)	120 (7)	25 (5)	71 (6)	5 (6)
C(17)	−0·0825 (6)	0·6922 (8)	0·0243 (2)	56 (5)	61 (6)	28 (4)	7 (5)	16 (4)	−1 (4)
C(18)	0·2288 (6)	0·6965 (7)	0·0065 (2)	71 (5)	75 (6)	75 (6)	−6 (5)	40 (5)	−20 (5)
N(11)	0·0731 (4)	0·8942 (5)	0·1009 (1)	45 (3)	44 (3)	33 (3)	5 (3)	19 (3)	−4 (3)
N(12)	0·1190 (4)	0·7061 (5)	0·1809 (1)	46 (3)	40 (4)	31 (3)	4 (3)	18 (3)	3 (3)
N(13)	−0·0680 (4)	0·5258 (5)	0·1041 (1)	36 (3)	56 (4)	35 (3)	8 (3)	12 (3)	0 (3)
N(14)	−0·1553 (4)	0·7518 (5)	0·0319 (1)	38 (3)	43 (3)	42 (3)	7 (3)	18 (3)	1 (3)
O(11)	−0·0828 (4)	0·9940 (4)	0·0851 (1)	62 (3)	63 (3)	42 (3)	25 (3)	25 (2)	9 (2)
O(12)	0·2436 (3)	0·7095 (4)	0·1596 (1)	48 (3)	42 (3)	55 (3)	−2 (2)	30 (2)	−7 (2)
O(13)	−0·0992 (4)	0·5922 (5)	0·1593 (1)	72 (3)	89 (4)	49 (3)	21 (3)	38 (3)	10 (3)
O(14)	−0·0955 (4)	0·5800 (5)	0·0138 (1)	64 (3)	52 (3)	54 (3)	−7 (3)	35 (3)	−13 (3)
C(21)	0·0882 (7)	0·8962 (7)	0·2532 (2)	66 (5)	55 (5)	39 (5)	0 (5)	25 (4)	3 (4)
C(22)	0·1597 (6)	0·8445 (7)	0·2448 (2)	58 (5)	51 (5)	39 (4)	1 (4)	24 (4)	−11 (4)
C(23)	0·1399 (5)	0·8376 (6)	0·1965 (2)	54 (4)	39 (5)	30 (4)	3 (4)	19 (3)	−6 (3)
C(24)	0·0408 (5)	0·9180 (6)	0·1633 (2)	36 (4)	42 (5)	30 (4)	3 (3)	12 (3)	−7 (3)
C(25)	−0·0284 (5)	0·9650 (6)	0·1747 (2)	53 (4)	42 (4)	39 (5)	0 (4)	24 (4)	−10 (3)
N(21)	−0·0084 (5)	0·9555 (5)	0·2186 (2)	70 (4)	61 (4)	40 (4)	16 (3)	37 (3)	3 (3)
C(31)	−0·2849 (9)	0·7380 (12)	0·2454 (3)	85 (8)	104 (10)	115 (9)	−10 (7)	55 (7)	21 (8)
C(32)	−0·2048 (10)	0·6990 (9)	0·2390 (4)	106 (9)	71 (8)	180 (12)	21 (7)	90 (9)	23 (7)
C(33)	−0·1431 (7)	0·7823 (10)	0·2316 (3)	75 (6)	76 (7)	128 (8)	7 (6)	70 (6)	2 (6)
C(34)	−0·1604 (6)	0·9080 (8)	0·2315 (2)	63 (5)	59 (6)	44 (4)	−2 (4)	29 (4)	−9 (4)
C(35)	−0·2452 (7)	0·9469 (8)	0·2368 (2)	64 (5)	58 (6)	78 (6)	4 (5)	38 (5)	−10 (5)
C(36)	−0·3049 (7)	0·8604 (12)	0·2437 (3)	68 (6)	106 (9)	102 (8)	1 (7)	54 (6)	−14 (7)
C(41)	0·0967 (7)	0·2845 (7)	0·1091 (2)	62 (5)	31 (5)	53 (5)	4 (4)	20 (4)	−7 (4)
C(42)	0·0334 (6)	0·3259 (7)	0·1231 (2)	50 (5)	37 (5)	71 (5)	1 (4)	27 (4)	−2 (4)
C(43)	0·0371 (5)	0·4593 (6)	0·1388 (2)	37 (4)	48 (5)	40 (4)	5 (4)	16 (3)	1 (4)
C(44)	0·1349 (5)	0·5249 (6)	0·1425 (2)	42 (4)	35 (4)	43 (4)	8 (4)	22 (4)	−6 (3)
C(45)	0·1918 (5)	0·4741 (6)	0·1261 (2)	50 (4)	29 (5)	38 (4)	1 (4)	15 (4)	−1 (3)
N(41)	0·1750 (5)	0·3574 (6)	0·1080 (2)	56 (4)	45 (4)	50 (4)	5 (3)	29 (3)	3 (3)
C(51)	0·5200 (10)	0·1374 (15)	0·2317 (4)	72 (8)	172 (14)	76 (8)	36 (10)	24 (6)	−15 (10)
C(52)	0·5241 (8)	0·2601 (14)	0·2225 (4)	37 (6)	159 (12)	100 (9)	6 (8)	14 (6)	−55 (10)
C(53)	0·4405 (8)	0·3104 (9)	0·1804 (4)	60 (6)	84 (7)	113 (8)	−10 (6)	38 (6)	−48 (7)
C(54)	0·3527 (6)	0·2384 (9)	0·1475 (2)	54 (5)	72 (6)	55 (5)	13 (5)	30 (5)	−6 (5)
C(55)	0·3511 (7)	0·1159 (10)	0·1574 (3)	66 (6)	73 (7)	82 (7)	8 (6)	14 (5)	14 (6)
C(56)	0·4339 (10)	0·0638 (11)	0·1994 (4)	94 (8)	114 (10)	94 (8)	18 (8)	25 (7)	28 (8)
C(61)	−0·4036 (6)	0·8077 (8)	0·0193 (3)	44 (5)	84 (7)	82 (6)	14 (5)	23 (5)	12 (5)
C(62)	−0·3553 (6)	0·7494 (8)	0·0015 (2)	44 (5)	89 (7)	52 (5)	6 (5)	15 (4)	0 (5)
C(63)	−0·2453 (5)	0·6828 (7)	0·0320 (2)	37 (4)	56 (5)	50 (5)	0 (4)	17 (3)	−10 (4)
C(64)	−0·2182 (5)	0·6706 (7)	0·0819 (2)	41 (4)	55 (5)	40 (4)	1 (4)	19 (4)	2 (4)
C(65)	−0·2733 (5)	0·7387 (7)	0·0958 (2)	47 (4)	63 (5)	63 (5)	10 (4)	34 (4)	2 (4)
N(61)	−0·3625 (4)	0·8124 (5)	0·0670 (2)	64 (4)	64 (4)	83 (4)	18 (3)	47 (4)	1 (4)
C(71)	−0·3123 (8)	1·2642 (8)	0·1191 (3)	74 (6)	77 (7)	70 (6)	22 (6)	28 (5)	−14 (5)
C(72)	−0·3867 (8)	1·2149 (11)	0·1279 (3)	73 (7)	107 (9)	88 (7)	28 (7)	46 (6)	−10 (7)
C(73)	−0·4199 (7)	1·0926 (11)	0·1170 (3)	74 (6)	107 (8)	67 (6)	29 (6)	46 (5)	2 (6)
C(74)	−0·3801 (6)	1·0187 (7)	0·0957 (2)	46 (5)	71 (6)	61 (5)	12 (4)	26 (4)	4 (4)
C(75)	−0·3063 (7)	1·0700 (9)	0·0861 (2)	63 (5)	72 (7)	69 (6)	21 (5)	40 (5)	2 (5)
C(76)	−0·2729 (6)	1·1942 (10)	0·0974 (2)	53 (5)	87 (7)	59 (5)	15 (5)	20 (4)	11 (4)
C(81)	0·1835 (6)	0·8859 (7)	0·0329 (2)	76 (6)	47 (5)	38 (4)	−14 (4)	32 (4)	−2 (4)
C(82)	0·1283 (6)	0·9502 (7)	0·0470 (2)	69 (5)	52 (5)	41 (4)	0 (4)	28 (4)	−1 (4)
C(83)	0·0373 (5)	0·8959 (7)	0·0508 (2)	52 (5)	50 (5)	26 (4)	4 (4)	14 (3)	−6 (3)
C(84)	0·0102 (5)	0·7657 (6)	0·0302 (2)	42 (4)	41 (4)	27 (4)	8 (4)	13 (3)	1 (3)
C(85)	0·0741 (6)	0·7075 (6)	0·0178 (2)	50 (4)	48 (5)	39 (4)	−5 (4)	20 (4)	−7 (4)
N(81)	0·1612 (5)	0·7636 (6)	0·0198 (2)	52 (4)	53 (4)	59 (4)	−5 (3)	30 (3)	−16 (3)
C(91)	0·5445 (9)	0·5687 (11)	0·1208 (5)	82 (8)	88 (9)	145 (12)	16 (7)	47 (9)	11 (9)
C(92)	0·5143 (10)	0·5538 (10)	0·0751 (5)	87 (9)	77 (8)	180 (13)	11 (7)	86 (10)	−3 (9)
C(93)	0·4119 (8)	0·5958 (8)	0·0390 (3)	71 (6)	74 (7)	106 (8)	−8 (6)	52 (6)	−29 (6)
C(94)	0·3395 (6)	0·6539 (7)	0·0481 (3)	70 (6)	53 (5)	92 (7)	−14 (4)	57 (5)	−20 (5)
C(95)	0·3701 (7)	0·6684 (8)	0·0942 (3)	73 (6)	59 (6)	84 (6)	−1 (5)	48 (5)	6 (5)
C(96)	0·4734 (10)	0·6267 (9)	0·1306 (3)	92 (8)	84 (8)	101 (8)	8 (7)	46 (7)	9 (6)

Table 3 (*cont.*)

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
H(11)	0·138 (4)	0·845 (5)	0·120 (1)	3 (1)	H(45)	0·255 (4)	0·525 (5)	0·128 (1)	2 (1)
H(12)	0·062 (4)	0·664 (5)	0·180 (1)	3 (2)	H(51)	0·574 (5)	0·097 (7)	0·262 (2)	9 (2)
H(13)	−0·088 (4)	0·526 (5)	0·075 (2)	4 (2)	H(52)	0·585 (5)	0·309 (6)	0·246 (2)	7 (2)
H(14)	−0·142 (4)	0·835 (5)	0·043 (2)	4 (2)	H(53)	0·451 (5)	0·403 (7)	0·175 (2)	8 (2)
H(15)	−0·137 (4)	1·070 (5)	0·204 (2)	4 (2)	H(55)	0·289 (6)	0·068 (7)	0·135 (2)	11 (3)
H(16)	−0·044 (4)	1·055 (5)	0·258 (2)	3 (1)	H(56)	0·431 (6)	−0·024 (7)	0·204 (2)	10 (3)
H(17)	0·289 (4)	0·361 (5)	0·092 (1)	1 (1)	H(61)	−0·472 (4)	0·856 (5)	−0·002 (2)	4 (2)
H(18)	0·220 (4)	0·236 (5)	0·074 (1)	3 (1)	H(62)	−0·384 (5)	0·746 (6)	−0·032 (2)	6 (2)
H(19)	−0·499 (5)	0·878 (6)	0·060 (2)	5 (2)	H(63)	−0·247 (4)	0·596 (4)	0·020 (1)	1 (1)
H(110)	−0·394 (5)	0·845 (6)	0·116 (2)	6 (2)	H(65)	−0·243 (4)	0·742 (5)	0·133 (1)	3 (1)
H(111)	0·228 (4)	0·758 (5)	−0·017 (2)	4 (2)	H(71)	−0·285 (4)	1·356 (5)	0·127 (2)	4 (2)
H(112)	0·189 (4)	0·627 (5)	−0·013 (1)	2 (1)	H(72)	−0·419 (5)	1·267 (6)	0·141 (2)	7 (2)
H(21)	0·098 (4)	0·890 (5)	0·285 (1)	1 (1)	H(73)	−0·474 (5)	1·055 (6)	0·123 (2)	6 (2)
H(22)	0·227 (4)	0·804 (5)	0·270 (1)	2 (1)	H(75)	−0·275 (4)	1·018 (5)	0·072 (1)	3 (1)
H(23)	0·211 (3)	0·864 (4)	0·199 (1)	0 (1)	H(76)	−0·223 (4)	1·236 (5)	0·090 (1)	4 (2)
H(25)	−0·098 (4)	1·011 (5)	0·150 (1)	2 (1)	H(81)	0·244 (4)	0·930 (5)	0·029 (2)	4 (2)
H(31)	−0·332 (5)	0·676 (6)	0·252 (2)	6 (2)	H(82)	0·144 (4)	1·042 (5)	0·054 (2)	5 (2)
H(32)	−0·184 (5)	0·608 (7)	0·241 (2)	8 (2)	H(83)	−0·031 (3)	0·950 (4)	0·034 (1)	0 (1)
H(33)	−0·090 (6)	0·752 (7)	0·228 (2)	8 (2)	H(85)	0·059 (4)	0·614 (5)	0·005 (1)	3 (1)
H(35)	−0·264 (5)	1·041 (6)	0·231 (2)	7 (2)	H(91)	0·622 (6)	0·541 (7)	0·149 (2)	10 (3)
H(36)	−0·361 (5)	0·894 (6)	0·248 (2)	6 (2)	H(92)	0·571 (5)	0·516 (6)	0·070 (2)	7 (2)
H(41)	0·092 (3)	0·197 (4)	0·098 (1)	0 (1)	H(93)	0·388 (5)	0·584 (6)	0·005 (2)	7 (2)
H(42)	−0·024 (4)	0·271 (5)	0·122 (2)	4 (2)	H(95)	0·315 (5)	0·706 (6)	0·100 (2)	6 (2)
H(43)	0·040 (4)	0·466 (5)	0·170 (1)	3 (1)	H(96)	0·501 (5)	0·654 (6)	0·166 (2)	5 (2)

thesis showed no electron density greater than 0·2 e Å^{-3} and no significant trends. The fractional coordinates and thermal parameters are given in Table 3.*

Description and discussion of the structure

A planar representation of the BNA molecule is shown in Fig. 1. Each hexagonal ring is labelled with a number; the remaining atoms of the molecule (*i.e.* >C=O, >N–H and methylene groups) are labelled as belonging to ring number 1.

Fig. 2 shows the shape of the molecule in the crystal. Each atom is labelled with two numbers; the first corresponds to the ring in which it belongs and the second differentiates atoms in the same ring. For the sake of clarity no H atoms are represented.

The central ring of the molecule presents a puckered conformation as can be seen from Fig. 2 (bold lines). Attached to the central ring are the four dihydropyridine rings. Ring 2 is approximately parallel to ring 6 (12°) and perpendicular to rings 4 (88°) and 8 (88°), which are almost parallel (6°). This situation gives rise to an intramolecular channel of cross-section ~3·7 × 3·7 Å^2 (calculated from the distances between planes of rings 2 and 6, and rings 4 and 8 respectively).

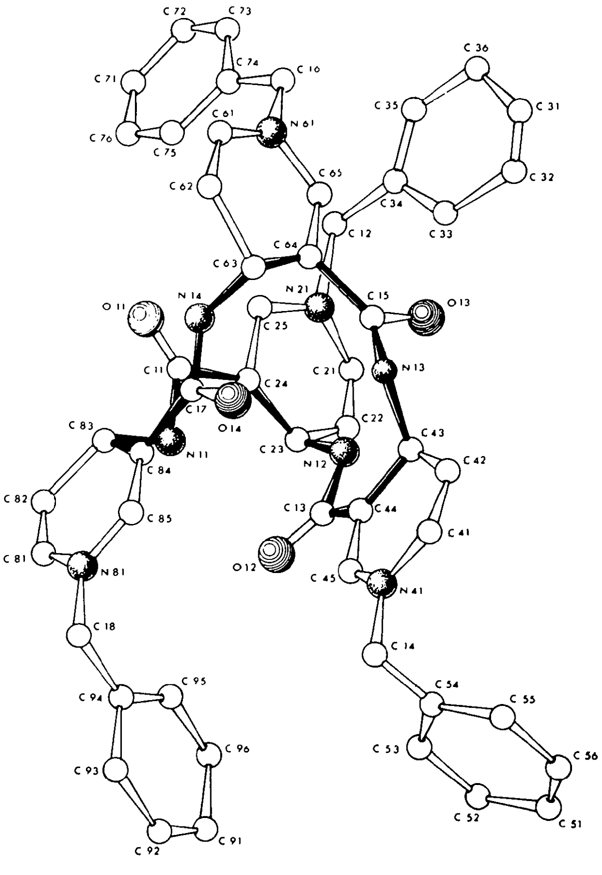

Fig. 2. BNA: molecular conformation.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32072 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bond lengths and angles*

(*a*) Averaged bond lengths and bond angles. The atom labelling corresponds to the monomer shown in the lower left of Fig. 2. Mean values and their standard errors have been calculated with the formulae:

$$x_m = \frac{\Sigma(x_i/\delta_i^2)}{\Sigma(1/\delta^2_i)}\ ; \qquad \sigma_m = \frac{1}{\sqrt{\Sigma(1/\delta_i^2)}}$$

where σ_m is a measure of the internal consistency of the data. Averaged least-squares standard errors are:

	Bond lengths	Bond angles
Involving non-H atoms	0·01 Å	0·8°
Involving H atoms	0·07	4

C(63)–N(14)	1·487 (5) Å	N(14)–H(14)	0·96 (3) Å
N(14)–C(17)	1·363 (7)	C(83)–H(83)	1·01 (3)
C(17)–O(14)	1·240 (5)	C(85)–H(85)	1·04 (3)
C(17)–C(84)	1·476 (5)	C(81)–H(81)	1·01 (3)
C(84)–C(85)	1·343 (7)	C(82)–H(82)	0·97 (3)
C(85)–N(81)	1·359 (5)	C(18)–H(111)	1·01 (2)
N(81)–C(81)	1·382 (6)	C(18)–H(112)	1·01 (2)
C(81)–C(82)	1·319 (8)	C(95)–H(95)	0·99 (3)
C(82)–C(83)	1·510 (6)	C(96)–H(96)	0·99 (3)
C(83)–C(84)	1·515 (5)	C(91)–H(91)	1·03 (3)
N(81)–C(18)	1·467 (7)	C(92)–H(92)	0·99 (3)
C(18)–C(94)	1·505 (6)	C(93)–H(93)	0·99 (3)
C(94)–C(95)	1·378 (5)		
C(95)–C(96)	1·380 (5)		
C(96)–C(91)	1·364 (7)		
C(91)–C(92)	1·364 (7)		
C(92)–C(93)	1·380 (5)		
C(93)–C(94)	1·378 (5)		

C(63)–N(14)–C(17)	121·2 (3)°	C(63)–N(14)–H(14)	117 (2)°
N(14)–C(17)–O(14)	121·0 (4)	H(14)–N(14)–C(17)	121 (2)
O(14)–C(17)–C(84)	122·2 (5)	C(84)–C(85)–H(85)	120 (2)
C(17)–C(84)–C(83)	122·7 (4)	H(85)–C(85)–N(81)	116 (2)
C(17)–C(84)–C(85)	115·4 (4)	N(81)–C(81)–H(81)	115 (2)
C(83)–C(84)–C(85)	121·6 (3)	H(81)–C(81)–C(82)	122 (2)
C(84)–C(85)–N(81)	123·7 (4)	C(81)–C(82)–H(82)	122 (2)
C(85)–N(81)–C(81)	117·7 (4)	H(82)–C(82)–C(83)	115 (2)
C(85)–N(81)–C(18)	120·8 (3)	C(82)–C(83)–H(83)	111 (2)
C(18)–N(81)–C(81)	120·7 (4)	N(11)–C(83)–H(83)	106 (2)
N(81)–C(81)–C(82)	123·5 (4)	H(83)–C(83)–C(84)	111 (2)
C(81)–C(82)–C(83)	123·1 (4)	N(81)–C(18)–H(111)	107 (2)
C(82)–C(83)–C(84)	109·1 (4)	N(81)–C(18)–H(112)	107 (2)
C(82)–C(83)–N(11)	109·7 (3)	H(111)–C(18)–H(112)	105 (3)
N(11)–C(83)–C(84)	110·5 (3)	H(111)–C(18)–C(94)	112 (1)
N(81)–C(18)–C(94)	113·9 (4)	H(112)–C(18)–C(94)	112 (1)
C(18)–C(94)–C(95)	120·6 (3)	C(94)–C(95)–H(95)	120 (2)
C(18)–C(94)–C(93)	120·6 (3)	H(95)–C(95)–C(96)	120 (2)
C(93)–C(94)–C(95)	118·8 (4)	C(95)–C(96)–H(96)	120 (2)
C(94)–C(95)–C(96)	120·5 (4)	H(96)–C(96)–C(91)	120 (2)
C(95)–C(96)–C(91)	120·1 (4)	C(96)–C(91)–H(91)	120 (2)
C(96)–C(91)–C(92)	120·3 (5)	H(91)–C(91)–C(92)	120 (2)
C(91)–C(92)–C(93)	120·1 (4)	C(91)–C(92)–H(92)	120 (2)
C(92)–C(93)–C(94)	120·5 (4)	H(92)–C(92)–C(93)	120 (2)
		C(92)–C(93)–H(93)	120 (2)
		H(93)–C(93)–C(94)	120 (2)

(*b*) Individual bond lengths within the dihydropyridine rings. Standard deviation for each value is 0·01 Å.

Ring 2		Ring 4		Ring 6		Ring 8	
C(23)–C(24)	1·51 Å	C(43)–C(44)	1·51 Å	C(63)–C(64)	1·52 Å	C(83)–C(84)	1·52 Å
C(23)–C(22)	1·51	C(43)–C(42)	1·52	C(63)–C(62)	1·51	C(83)–C(82)	1·50
C(25)–C(24)	1·35	C(45)–C(44)	1·33	C(65)–C(64)	1·34	C(85)–C(84)	1·35
C(21)–C(22)	1·33	C(41)–C(42)	1·31	C(61)–C(62)	1·31	C(81)–C(82)	1·33
N(21)–C(25)	1·36	N(41)–C(45)	1·36	N(61)–C(65)	1·36	N(81)–C(85)	1·36
N(21)–C(21)	1·39	N(41)–C(41)	1·39	N(61)–C(61)	1·39	N(81)–C(81)	1·37

The four benzene rings are attached to the dihydropyridine rings through methylene groups. The angles between the rings 2–3, 4–5, 6–7 and 8–9 are 68, 84, 81 and 79° respectively. While benzene rings 7 and 3 are roughly parallel (23°), rings 5 and 9 are almost perpendicular (79°), as can be seen from Fig. 2.

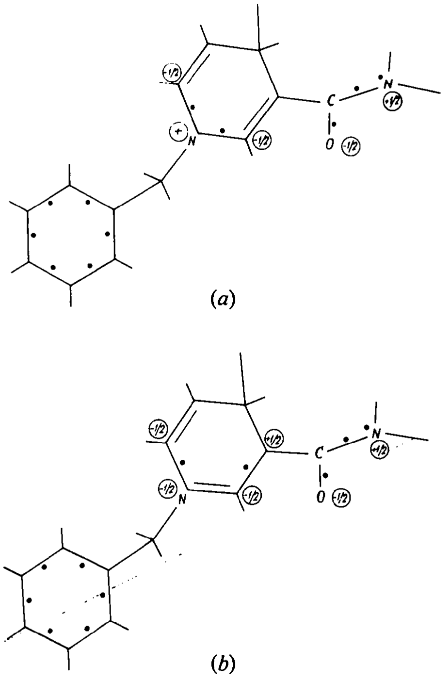
Each amidic fragment of the central ring is almost coplanar with the dihydropyridine ring, the O atom being at the *cis* position with respect to the N atom of the ring. The four asymmetric C atoms of the dihydropyridine rings [C(23), C(43), C(63), C(83)] present alternately *R* and *S* configurations (Fig. 2).

Table 4(*a*) shows the mean intramolecular distances and angles with their standard deviations.

Four intramolecular hydrogen bonds have been detected between the O atoms and the H atoms of the amidic fragments. Table 5 shows the geometry of these bonds. These may explain the lipophilic properties and the stability of the molecule, and help the formation of the above-mentioned intramolecular channel.

Table 5. *Geometry of the hydrogen bonds*

	N–H	N···O	H···O	N–H···O
N(11)–H(11)···O(12)	0·95 Å	2·92 Å	2·00 Å	164°
N(12)–H(12)···O(13)	0·92	3·05	2·16	164
N(13)–H(13)···O(14)	0·87	2·93	2·10	159
N(14)–H(14)···O(11)	0·95	3·01	2·09	164



(*a*)

(*b*)

Fig. 3. BNA: (*a*) major and (*b*) minor electron distributions in one of the monomers.

The geometry of the molecule suggests the electron distribution shown in Fig. 3(*a*) according to Linnett's (1966) theory. This model, the major distribution in the structure, would imply planarity of the dihydropyridine rings. However, this planarity is systematically disturbed by all the sp^3 C atoms, which are out of the plane in the direction of the adjacent N atoms, as shown in Table 6 (atoms with an asterisk were not included in the calculation of the planes). This lack of planarity could be explained by assuming the minor electron distribution shown in Fig. 3(*b*). This distribution would imply different bond lengths in the ring on each side of the hypothetical line N(X1)–C(X3) which indeed are systematically observed; that is, there is a shortening of the N(X1)–C(X5) bonds and a lengthening of the C(X5)–C(X4) bonds, with X = 2, 4, 6, 8 [Table 4(*b*)]. There is no significant difference around the asymmetric carbon atoms, C(X3), but there is around the N(X1) atoms, the difference between double bonds being possibly significant (on the basis of the usual probability level; *International Tables for X-ray Crystallography*, 1959).

The proposed electron distributions shown in Fig. 3 imply pyramidal geometry at the N atoms of the amidic fragments, which is supported by Ramachandran, Lakshminarayanan & Kolaskar (1973). However, this distribution is disturbed in that the deviations of the H atoms from the amidic planes range from 0·07 to 0·17 Å (the expected value being 0·24 Å). This could be due to hydrogen bonding (Table 5). Anyway, the bond lengths around the N atoms which imply the proposed electron distribution appear to us more conclusive than any consideration about the position of the H atoms.

All intermolecular distances are within the van der Waals limits (greater than 3·28 Å).

Most of the calculations were performed with the X-RAY 70 system of crystallographic programs

Table 6. *Deviations from ring planes*

Ring 2		Ring 4	
C(21)	0·01 Å	C(41)	0·03 Å
C(22)	−0·01	C(42)	−0·02
C(24)	0·01	C(44)	0·00
C(25)	0·00	C(45)	0·01
N(21)	−0·01	N(41)	−0·02
*C(23)	−0·15	*C(43)	−0·14
*N(12)	−1·49	*N(13)	−1·47

Ring 6		Ring 8.	
C(61)	−0·04 Å	C(81)	−0·02 Å
C(62)	0·02	C(82)	0·02
C(64)	0·00	C(84)	−0·01
C(65)	−0·01	C(85)	0·00
N(61)	0·03	N(81)	0·02
*C(63)	0·21	*C(83)	0·12
*N(14)	1·57	*N(11)	1·42

(Stewart, Kundell & Baldwin, 1970). We wish to thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia, Spain, for the facilities provided on the 1108 Univac computer. We gratefully acknowledge the valuable comments of Dr Fayos.

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The Crystal and Molecular Structure of 6-Acetyl-8-(acetyloxyimino)-2-phenyl-4-oxo-4,8-dihydro-2*H*,6*H*-pyrazolo[3,4-*f*]-1,2,3-benzotriazole–Dioxane (2:1)

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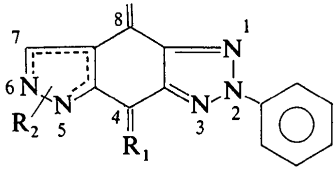
Crystals of the title compound are triclinic ($P\bar{1}$) with $a = 10{\cdot}457(5)$, $b = 9{\cdot}654(5)$, $c = 10{\cdot}207(4)$ Å; $\alpha = 78{\cdot}9(1)$, $\beta = 89{\cdot}9(1)$, $\gamma = 110{\cdot}3(1)°$; $Z = 2$. The structure, determined from diffractometer data by direct methods, was refined by block-diagonal least squares to $R = 5{\cdot}2\%$ for 1880 independent reflexions. The compound is a derivative of the new heterocycle pyrazolo[3,4-*f*]-1,2,3-benzotriazole and the analysis shows that the acetyl substituent is at N(6). Packing is essentially determined by a C–H $\cdots$ O contact, involving the dioxane molecule, which fulfils the geometrical requirements for a hydrogen bond.

Introduction

The reaction of diazomethane with 5-hydroxy-4-phenylbenzofurazan as a synthetic route to derivatives of the new heterocycle pyrazolo[3,4-*f*]-1,2,3-benzotriazole has been investigated by Cerè, Pollicino, Sandri & Scapini (1977), who have synthesized 2-phenyl-5(6)*H*-pyrazolo[3,4-*f*]-benzotriazole-4,8-dione and its mono- and dioximes of general formula



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The position of the R_2 substituent was not known, as it was not possible to ascertain by conventional chemical and spectroscopic methods whether N(5) or N(6) was substituted.

The structure of the derivative corresponding to $R = NOAc$, $R_1 = O$, $R_2 = Ac$ has been determined to elucidate the structural features of this class of compound, and in particular to define the position of the R_2 substituent.

Experimental

The title compound was obtained as crystals suitable for X-ray analysis from a toluene–dioxane (1:1) solution. The crystals contain solvent in the dioxane:com-