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Structure of 2-(Benzoylaminomethyl)-1-methyl-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepine Hydrochloride

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Abstract. $C_{24}H_{24}N_3O^+.Cl^-$, $M_r = 405.93$, orthorhombic, $Pna2_1$, $a = 15.373$ (16), $b = 22.223$ (12), $c = 6.267$ (4) Å, $V = 2141$ (3) Å^3, $Z = 4$, $D_m = 1.26$, $D_x = 1.26$ Mg m^{-3}, graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 1.729$ mm^{-1}, $F(000) = 856$, $T = 293$ K, final $R = 0.039$ for 2314 unique observed reflections. The absolute structure with respect to the polar axis was determined. The geometry of the benzodiazepine framework in the title compound is compared with other 2,3-dihydro-1*H*-1,4-benzodiazepines. The seven-membered ring adopts a conformation halfway between a distorted boat and a distorted sofa. The benzamide moiety of the axial 2-substituent has a geometry similar to common (di)benzamides. Two intramolecular hydrogen bonds link N(4) and the amidic N(12) with the chloride anion. Three intermolecular distances are smaller than the usual van der Waals interactions. A network of non-bonded intermolecular aromatic–aromatic interactions is formed between the molecules.

Introduction. Since it has been shown that the 2-acylaminomethylbenzodiazepine tifluadom is selective for opioid κ receptors (Romer, Buscher, Hill, Maurer, Petcher, Zeugner, Benson, Finner, Milkowski & Thies, 1982), it seemed worthwhile to determine the crystal structure of the title compound as part of a structure–activity study on benzodiazepine derivatives with opioid activity.

Experimental. Orange crystals (from ethyl acetate–acetone), 0.7 × 0.4 × 0.03 mm. Density measured by flotation in *n*-heptane/CCl_4. The X-ray measurements were carried out on a Stoe Stadi-4 diffractometer. Cell parameters were determined by least-squares refinement of the setting angles of 30 reflections with $30 \le 2\theta \le 40°$. Intensities measured by ω–2θ scans, $(\sin\theta/\lambda)_{max} = 0.5878$ Å^{-1}, h 0 to 18, k −26 to 26, l −7 to 7. Crystal decay was checked by monitoring intensities of four standard reflections (060, 410, 201, 002) every hour. The average decrease was 2.6% for the total measuring time; decay correction applied. 6439 reflections were measured (3087 unique, Friedel pairs hkl and $hk\bar{l}$ not averaged, $R_{int} = 0.050$), 2318 reflections with $I \ge 3\sigma(I)$. Data reduction was performed with the locally adapted *REDU*4 program (Stoe & Co., 1985). Absorption corrections were performed according to the method of North, Phillips & Mathews (1968); the minimum and maximum transmission factors were 0.25 and 0.42 respectively. Lorentz and polarization corrections were applied. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968), those for H atoms from Stewart, Davidson & Simpson (1965). The anomalous-dispersion factors for C, N, O and Cl were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). The structure was solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on F with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) by full-matrix least squares with fixed z position of the chloride atom. Isotropic refinement converged to $R = 0.104$. At this stage H atoms were located from a difference Fourier synthesis but placed in calculated geometrical positions (C—H and N—H = 0.95 Å) and assigned an isotropic temperature factor 1.3 times that of the parent atom. Also at this stage the orientation of the structure with respect to the polar axis was determined by calculating the Bijvoet coefficient according to a selection procedure by Beurskens, Noordik & Beurskens (1980). It appeared to be necessary to invert the structure. Four of the highest reflection intensities suffering badly from extinction were rejected. Further anisotropic refinement with fixed parameters for the H atoms converged to $R = 0.039$ ($wR = 0.050$), $S = 1.052$. The quantity minimized was $\sum w|\Delta F|^2$, with $w = (\sigma_F^2 + 0.0016|F_o|^2)^{-1}$. The average and maximum shift to e.s.d. ratios for the final cycle were 0.0096 and 0.035.

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The final difference Fourier synthesis showed no significant features (minimum and maximum residual electron density -0.39 and 0.33 e Å^{-3}). At the end of the refinement the final Bijvoet coefficient was 0.945 (2) from the largest 364 Friedel pairs. These pairs were selected using the parameters $N = 1$, $N' = 2$; for larger values of N and N' the Bijvoet coefficient is between 0.9753 (9) and exactly 1. The program *PARST* (Nardelli, 1983) was used for the geometrical calculations.

Discussion. An *ORTEP* (Johnson, 1965) view of the molecule with the atom numbering following that of tifluadom hydrochloride (Petcher, Widmer, Maetzel & Zeugner, 1985) is shown in Fig. 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths, bond angles and selected torsion angles are listed in Table 2.* Table 3 compares some features of the benzodiazepine fragment of the title compound (1) with related 2,3-dihydro-1*H*-1,4-benzodiazepines (Fig. 2).

Benzodiazepine framework. The three-dimensional view of the heptadiene ring in the title compound ressembles more the other 2-acylamido derivatives [Table 3: compounds (2), (3) and (4)] than the medazepam molecules [Table 3: compounds (5), (6) and (7)]. The substitution of the H atom at C(2) in medazepam by a 2-acylamido substituent seems to affect significantly the conformation of the diazepine ring and the configuration of N(1). The seven-membered ring adopts a conformation halfway between a distorted boat and a distorted sofa (see puckering parameters in Table 3*e*) (Boessenkool & Boeyens, 1980) whereas the medazepam molecules have more of a distorted boat conformation. The substitution of H(2) in medazepam by a 2-acylamido substituent causes a significant flattening of the stern part of the boat (see stern angle in Table 3*d*: ∠*BC*). This flattening relates to the configurational change of the N(1) atom, being tetrahedral in the medazepam molecules and trigonal in the 2-acylamido derivatives. This trigonal character of N(1) is expressed by the three following features. First the 2-acylamido derivatives have a decreased dihedral angle between the benzene [C(5a)–C(9a)] and the C(10)N(1)C(2) plane (Table 3*d*: ∠*AE*). Secondly the endocyclic angle C(9a)—N(1)—C(2) is much increased (Table 3*b*). Finally the C(9a)—N(1) bond length ressembles more the C(ar)—N(3) length for an N(sp^2) configuration [Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987; 1.371 (16) Å] than for an N(sp^3) pyramidal configuration [Allen *et al.*, 1987; 1.426 (11) Å]. These features at N(1) suggest a certain electron delocalization between the benzene [C(5a)–C(9a)] and N(1).

The distortion of the basis plane N(1)C(2)N(4)C(5) is quite similar in all the seven heptadiene derivatives (see pseudo torsion angles in Table 3*c*). The C(5)—C(1′) bond has a normal C(*ar*)—C(sp^2) value [Allen *et al.*, 1987; 1.485 (13) Å] and is similar for all compounds. In the 2-acylamido

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Cl	7913.1 (6)	5963.9 (4)	4523*	5.78 (2)
N(1)	6380 (1)	4170 (1)	9029 (5)	4.29 (8)
C(2)	6302 (2)	4762 (1)	8026 (5)	3.69 (8)
C(3)	6468 (2)	4746 (1)	5673 (5)	3.75 (8)
N(4)	7394 (1)	4680 (1)	5199 (4)	3.66 (7)
C(5)	7821 (2)	4195 (1)	5589 (5)	3.51 (8)
C(5a)	7425 (2)	3662 (1)	6536 (6)	3.79 (8)
C(6)	7765 (2)	3108 (1)	5843 (7)	4.97 (10)
C(7)	7479 (2)	2568 (1)	6580 (8)	5.72 (12)
C(8)	6856 (2)	2571 (1)	8159 (9)	5.96 (12)
C(9)	6504 (2)	3096 (1)	8903 (6)	5.17 (11)
C(9a)	6753 (2)	3668 (1)	8120 (6)	3.92 (9)
C(10)	5753 (3)	4085 (2)	10740 (7)	6.46 (13)
C(11)	6849 (2)	5229 (1)	9217 (6)	4.40 (9)
N(12)	6630 (1)	5836 (1)	8578 (5)	4.45 (8)
C(13)	5931 (2)	6119 (1)	9380 (7)	4.64 (9)
O(14)	5472 (1)	5878 (1)	10752 (5)	6.12 (8)
C(15)	5724 (2)	6721 (1)	8498 (7)	4.68 (10)
C(16)	5050 (2)	7046 (1)	9442 (8)	6.29 (13)
C(17)	4781 (2)	7589 (2)	8604 (11)	7.29 (17)
C(18)	5159 (3)	7823 (2)	6842 (10)	6.87 (15)
C(19)	5835 (3)	7510 (2)	5887 (8)	6.82 (14)
C(20)	6117 (2)	6968 (1)	6722 (8)	5.87 (12)
C(1′)	8766 (2)	4199 (1)	5034 (6)	3.65 (8)
C(2′)	9053 (2)	4442 (1)	3138 (7)	4.51 (10)
C(3′)	9938 (2)	4449 (1)	2674 (7)	5.42 (12)
C(4′)	10512 (2)	4230 (1)	4142 (9)	5.92 (13)
C(5′)	10243 (2)	3999 (1)	6074 (8)	5.68 (13)
C(6′)	9358 (2)	3973 (1)	6511 (7)	4.68 (10)

* Parameter kept fixed for origin definition.

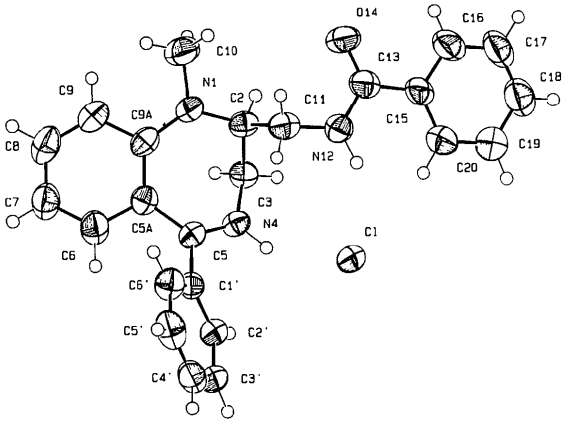


Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule with 50% probability thermal ellipsoids for the non-H atoms. The numbering of the H atoms is the same as that of the neighbouring C or N atoms.

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, least-squares planes, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54558 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

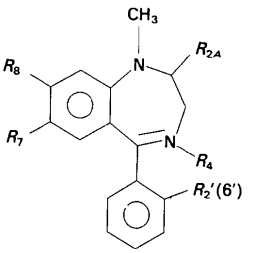
Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(2)	1.464 (4)	N(12)—C(13)	1.342 (4)
N(1)—C(9a)	1.378 (4)	C(13)—O(14)	1.234 (5)
N(1)—C(10)	1.454 (6)	C(13)—C(15)	1.483 (5)
C(2)—C(3)	1.497 (5)	C(15)—C(16)	1.393 (5)
C(2)—C(11)	1.530 (4)	C(15)—C(20)	1.380 (6)
C(3)—N(4)	1.462 (4)	C(16)—C(17)	1.380 (6)
N(4)—C(5)	1.285 (4)	C(17)—C(18)	1.351 (8)
C(5)—C(5a)	1.459 (4)	C(18)—C(19)	1.386 (7)
C(5)—C(1′)	1.493 (4)	C(19)—C(20)	1.383 (6)
C(5a)—C(6)	1.405 (4)	C(1′)—C(2′)	1.377 (5)
C(5a)—C(9a)	1.433 (5)	C(1′)—C(6′)	1.392 (5)
C(6)—C(7)	1.360 (5)	C(2′)—C(3′)	1.391 (5)
C(7)—C(8)	1.377 (7)	C(3′)—C(4′)	1.365 (6)
C(8)—C(9)	1.368 (5)	C(4′)—C(5′)	1.378 (7)
C(9)—C(9a)	1.4515 (5)	C(5′)—C(6′)	1.389 (5)
C(11)—N(12)	1.446 (4)		

C(2)—N(1)—C(9a)	125.8 (3)	C(2)—C(11)—N(12)	111.7 (2)
C(2)—N(1)—C(10)	112.3 (2)	C(11)—N(12)—C(13)	121.3 (3)
C(9a)—N(1)—C(10)	118.4 (3)	N(12)—C(13)—O(14)	121.0 (3)
N(1)—C(2)—C(3)	112.8 (2)	N(12)—C(13)—C(15)	117.1 (3)
N(1)—C(2)—C(11)	110.8 (2)	O(14)—C(13)—C(15)	121.8 (3)
C(3)—C(2)—C(11)	113.8 (2)	C(13)—C(15)—C(16)	117.9 (3)
C(2)—C(3)—N(4)	111.6 (2)	C(13)—C(15)—C(20)	124.3 (3)
C(3)—N(4)—C(5)	122.9 (2)	C(16)—C(15)—C(20)	117.6 (3)
N(4)—C(5)—C(5a)	123.0 (2)	C(15)—C(16)—C(17)	120.9 (4)
N(4)—C(5)—C(1′)	116.6 (2)	C(16)—C(17)—C(18)	121.2 (4)
C(5a)—C(5)—C(1′)	120.3 (2)	C(17)—C(18)—C(19)	118.8 (4)
C(5)—C(5a)—C(6)	115.5 (3)	C(18)—C(19)—C(20)	120.6 (4)
C(5)—C(5a)—C(9a)	125.1 (2)	C(15)—C(20)—C(19)	120.9 (4)
C(6)—C(5a)—C(9a)	119.3 (3)	C(5)—C(1′)—C(2′)	121.0 (3)
C(5a)—C(6)—C(7)	123.2 (3)	C(5)—C(1′)—C(6′)	118.6 (3)
C(6)—C(7)—C(8)	117.7 (3)	C(2′)—C(1′)—C(6′)	120.3 (3)
C(7)—C(8)—C(9)	121.6 (3)	C(1′)—C(2′)—C(3′)	119.9 (3)
C(8)—C(9)—C(9a)	122.7 (3)	C(2′)—C(3′)—C(4′)	119.1 (4)
N(1)—C(9a)—C(5a)	126.4 (3)	C(3′)—C(4′)—C(5′)	122.1 (3)
N(1)—C(9a)—C(9)	118.1 (3)	C(4′)—C(5′)—C(6′)	118.9 (3)
C(5a)—C(9a)—C(9)	115.3 (3)	C(1′)—C(6′)—C(5′)	119.7 (3)

C(9a)—N(1)—C(2)—C(3)	14.4 (6)	N(1)—C(2)—C(11)—N(12)	−166.6 (3)
N(1)—C(2)—C(3)—N(4)	−74.6 (4)	C(2)—C(11)—N(12)—C(13)	80.4 (5)
C(2)—C(3)—N(4)—C(5)	68.7 (5)	N(4)—C(5)—C(1′)—C(2′)	−42.9 (5)
C(3)—N(4)—C(5)—C(5a)	0.3 (6)	N(4)—C(5)—C(5a)—C(9a)	−35.7 (6)
C(5)—C(5a)—C(9a)—N(1)	−0.9 (7)	C(11)—N(12)—C(13)—O(14)	2.9 (6)
C(5a)—C(9a)—N(1)—C(2)	27.8 (6)	C(11)—N(12)—C(13)—C(15)	−175.6 (4)
C(9a)—N(1)—C(2)—C(11)	−114.5 (4)		

derivatives the C(5a)—C(5) distance is shortened as compared to medazepam (Table 3*a*). This points to a certain degree of electron delocalization between the benzene [C(5a)–C(9a)] and the adjacent C=N system.



	R_{2A}	R_4	R_7	R_8	R_2' (6′)
(1)	$-CH_2NHCOC_6H_5$	H^+	H	H	H
(2)	$-CH_2NHCOC_4H_3O$	H^+	H	Cl	H
(3)	$-CH_2NHCOC_4H_3S$	–	H	H	F
(4)	$-CH_2NHCOC_4H_3S$	H^+	H	H	F
(5), (6)	—H	–	Cl	H	H
(7)	—H	H^+	Cl	H	H

Fig. 2. Details of 2,3-dihydro-1*H*-1,4-benzodiazepines. (1) Title compound. (2) 8-Chloro-2-[(3-furoyl)aminomethyl]-1-methyl-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepine hydrochloride (Blaton, Vynckier, Verlinde, Peeters & De Ranter, 1988). (3) Tifluadom hydrate (Codding, Zeugner & Finner, 1987). (4) Tifluadom hydrochloride (Petcher *et al.*, 1985). (5), (6) Medazepam base, molecules *A* and *B* (Gilli *et al.*, 1978*b*). (7) Medazepam hydrochloride (Chananont, Hamor & Martin, 1980).

Table 3. *Comparison of selected features of the title compound with other* 2,3-*dihydro*-1*H*-1,4-*benzodiazepines*

The formulas of the molecules are as given in Fig. 2. In some cases the torsion angles are for the inverted molecule to facilitate comparison. The dihedral angles are acute angles.

	(1)	(2)	(3)*	(4)	(5)	(6)	(7)
(*a*) Bond lengths (Å)							
C(9a)—N(1)	1.378 (4)	1.369 (3)	1.402 (9)†	1.361 (3)†	1.388 (5)	1.398 (5)	1.406 (5)
C(5a)—C(5)	1.459 (5)	1.455 (3)	1.485 (10)†	1.448 (4)†	1.492 (5)	1.479 (5)	1.479 (5)
C(5)—C(1′)	1.493 (5)	1.475 (3)	1.489 (10)†	1.486 (4)†	1.488 (5)	1.492 (5)	1.483 (5)
(*b*) Bond angles (°)							
C(9a)—N(1)—C(2)	125.7 (3)	126.8 (3)†	123.7 (7)†	127.4 (2)†	120.6 (3)	118.9 (3)	119.6‡
C(3)—N(4)—C(5)	122.9 (3)	124.3 (3)†	115.8 (6)†	121.9 (3)†	115.8 (3)	116.6 (3)	123.0‡
(*c*) Pseudo torsion angles (°)							
N(1)—C(2)—N(4)—C(5)	10.3 (4)	10.2 (3)†	3.6 (7)†	7.0 (3)†	11.8 (4)†	14.4 (3)†	15.9 (4)†
(*d*) Dihedral angles (°)							
Plane *A* C(5a)C(6)C(7)C(8)C(9)C(9a)		Plane *B* N(1)C(9a)C(5a)C(5)			Plane *C* N(1)C(2)N(4)C(5)		
Plane *D* C(1′)C(2′)C(3′)C(4′)C(5′)C(6′)		Plane *E* C(10)N(1)C(2)					
∠AE	19.5 (2)	15.0 (2)†	31.1 (5)†	20.8 (2)†	45.7 (2)†	47.1 (2)†	49.6 (3)†
∠AB	2.8 (2)	2.6 (2)†	1.7 (3)†	2.8 (2)†	2.2 (2)†	3.2 (1)†	3.6 (2)†
∠BC	26.4 (2)	21.2 (2)†	34.6 (4)†	26.5 (2)†	43.8 (2)†	45.3 (2)†	45.8 (2)†
∠AD	67.4 (2)	58.3 (1)†	77.3 (2)†	69.6 (1)†	62.8 (1)†	55.4 (1)†	67.2 (1)†
(*e*) Puckering parameters							
q_2 (Å)	0.73	0.66†	0.84†	0.74†	0.95†	0.96†	0.95†
q_3 (Å)	0.26	0.29†	0.22†	0.27†	0.16†	0.15†	0.14†
φ_2 (°)	147	−34†	−28†	−31†	−17†	165†	−15†
φ_3 (°)	41	−139†	−131†	−136†	−111†	74†	−95†

* Care should be taken when interpreting the values for (3) because of their large e.s.d.'s.

† These values were missing from the original publications; they were calculated locally by the program *PARST* (Nardelli, 1983).

‡ Published values with e.s.d. 0.3 to 0.4.

In conformity with the VSEPR theory (Gillespie, 1970) protonation causes the widening of the endocyclic angle at N(4) (Table 3*b*). Other bond lengths and angles in the diazepine ring of the title compound are in accordance with the expected normal values.

The 5-phenyl and the [C(5a)—C(9a)] benzene rings deviate significantly from planarity (χ^2 27.3 and 43.6, respectively). The dihedral angle between these two rings [67.4 (2)°] lies in the range of values commonly encountered for benzodiazepines bearing an unsubstituted 5-phenyl ring [54.5 (1)° in oxazepam (molecule *A* in Gilli, Bertolasi, Sacerdoti & Borea, 1978*a*) to 71.1 (1)° in prazepam (Brachtel & Jansen, 1981)].

N-Methylbenzamide side chain. The *N*-methylbenzamide substituent on C(2) is axial [pseudo torsion angle C(5)—N(1)—C(2)—C(11) = −91.6 (3)°] and projected away from the benzodiazepine skeleton. The aromatic ring C(15)–C(20) is nearly parallel with the benzene C(5a)–C(9a) [26.5 (2)°]. The bond lengths of the amide part compare with reference values for acyclic amides (Allen *et al.*, 1987). The *Z* conformation of the amide part as well as the bond lengths and angles of the benzamide moiety compare with values found in (di)benzamides having an unsubstituted benzene and showing no through-conjugation between the benzamide part and the rest of the molecule [Cambridge Structural Database (CSD) search with $R < 6.0\%$ and mean e.s.d. of C—C bond lengths < 0.010 Å] (Table 4). In the title compound the amide lies close to the plane of the phenyl ring [11.0 (3)°].

In the title compound the chloride anion is hydrogen bonded to N(4) [Cl···N(4) = 2.993 (3), Cl···H(4) = 2.14 Å, ∠Cl···H(4)—N(4) = 149°] and N(12) [Cl···N(12) = 3.230 (4), Cl···H(12) = 2.37 Å, ∠Cl···H(12)—N(12) = 149°]. Intermolecular contacts shorter than the sum of the van der Waals radii occur between Cl—H(8)^{i} (2.86 Å), Cl—H(5)^{ii} (2.70 Å) and C(10)—C(15)^{iii} [3.370 (7) Å] [symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$; (ii) $2-x, 1-y, \frac{1}{2}+z$; (iii) $1-x, 1-y, \frac{1}{2}+z$].

The packing of the molecule is illustrated in Fig. 3. Non-bonded intermolecular interactions occur between the aromatic rings forming a network of eight aromatic–aromatic interactions per unit cell. The phenyl centroid separation varies from 4.48 (3) to 7.75 (8) Å. Three different types of stacking are present, namely the tilted type, the edge-ring face type and the cogwheel type (respectively for three, one and four ring–ring interactions in the unit cell) (Singh & Thornton, 1985).

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Table 4. *CSD search of benzamides*

Intermolecular hydrogen bonding motif: (*a*) twofold screw axis, or glide; (*b*) translation.

CSD code	Compound	Reference
(*a*)		
MBNZAM10	*N*-Methylbenzamide	(1)
ETBZAM	*N,N'*-Ethylenedibenzamide	(2)
(*b*)		
BAGYAU10	*N,N'*-Hexamethylenedibenzamide	(3)
CAHCIX	*N,N'*-Octamethylenedibenzamide	(4)
MEBZAM	*N,N'*-Tetramethylenedibenzamide	(5)

References: (1) Leiserowitz & Tuval (1978). (2) Palmer & Brisse (1980). (3) Pineault & Brisse (1983*a*). (4) Pineault & Brisse (1983*b*). (5) Harkema, van Hummel & Gaymans (1980).

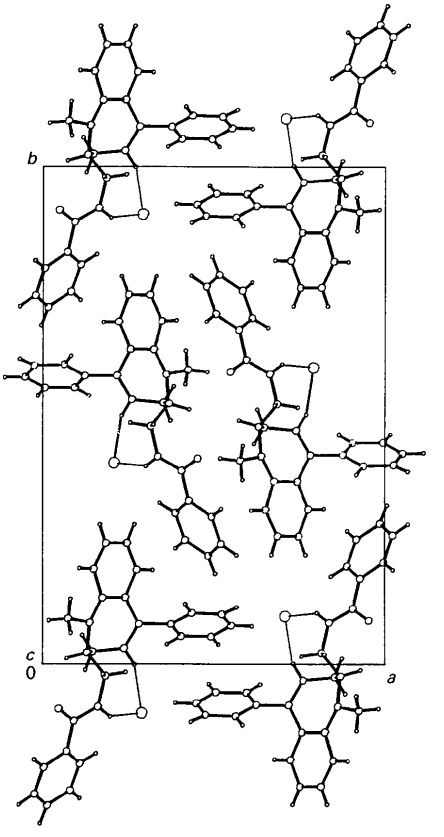

Fig. 3. A view of the crystal structure along **a** showing the packing (*PLUTO*; Motherwell & Clegg, 1978). Intramolecular hydrogen bonds are indicated by small lines.

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Structures of New DNA Photocleaving Agents: 3,6-Bis(dimethylamino)-10-[6-(4-nitrobenzoyloxy)hexyl]acridinium Chloride (I) and 9-{[6-(4-Nitrobenzoyloxy)-hexyl]amino}acridinium Chloride Monohydrate (II)

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Abstract. (I) $C_{30}H_{35}N_4O_4^+.Cl^-$, $M_r = 551.07$, triclinic, $P\bar{1}$, $a = 10.512\ (2)$, $b = 11.203\ (2)$, $c = 14.469\ (2)$ Å, $\alpha = 111.49\ (1)$, $\beta = 105.74\ (1)$, $\gamma = 95.82\ (1)°$, $V = 1487.4\ (4)$ Å^3, $Z = 2$, $D_m = 1.23$ (by flotation), $D_x = 1.231$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 14.68$ cm^{-1}, $F(000) = 584$, $T = 296$ K, $R = 0.109$ for 3100 unique reflections with $I > 3\sigma(I)$. (II) $C_{26}H_{26}N_3O_4^+.Cl^-.H_2O$, $M_r = 497.98$, triclinic, $P\bar{1}$, $a = 9.4810\ (8)$, $b = 14.495\ (2)$, $c = 9.255\ (1)$ Å, $\alpha = 95.48\ (1)$, $\beta = 98.17\ (1)$, $\gamma = 101.78\ (1)°$, $V = 1222.3\ (5)$ Å^3, $Z = 2$, $D_m = 1.35$ (by flotation), $D_x = 1.353$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 17.34$ cm^{-1}, $F(000) = 524$, $T = 296$ K, $R = 0.052$ for 3589 unique reflections with $I > 3\sigma(I)$. The diffraction work confirmed the molecular structures of the newly synthesized DNA photocleaving compounds, in which the *p*-nitrophenyl group is nearly coplanar with the acridine moiety in (I), whereas the two planar groups form a dihedral angle of 98.7° in (II). The flexibility of the methylene chain and the substantial stacking ability of the aromatic groups observed may be essential for binding to DNA and reaction with the deoxyribose H atoms.

Introduction. Synthetic agents which interact with DNA, particularly those possessing base sequence selectivity have recently attracted much interest (Dervan, 1986). We have designed and synthesized a new series of DNA photocleaving compounds and studied their interaction with DNA. The compounds consist of a *p*-nitrobenzoyl group which cleaves DNA on UV irradiation, and of an acridine moiety [acridine orange in compound (I), and 9-aminoacridine in (II)] which is a potential intercalator and is essential for the compounds' photocleavage activity (R. Kuroda & M. Shinomiya, to be published). Molecular and crystal structures of (I) and (II) have been determined in order to understand the possible mechanism of the interaction of these compounds with DNA.

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