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2-[3-(9-Acridinylamino)-propylamino]ethanol (ICR-449-OH), an Analogue of a Mutagen

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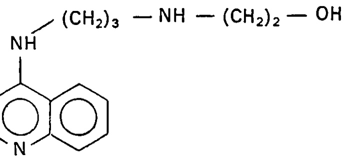
Crystals of 2-[3-(9-acridinylamino)-propylamino]ethanol (ICR 449–OH), $C_{18}N_3OH_{21}$, are monoclinic, space group $P2_1/a$ with $Z=4$, F.W. 295·4, cell dimensions $a=15·618$ (2), $b=10·281$ (1), $c=9·713$ (1) Å, $\beta=102·61°$ (1), $V=1522·0$ (3) Å^3. The calculated and measured densities are 1·29 and 1·27 g cm^{-3} respectively. The structural formula is:



Three-dimensional diffractometer data were collected with Cu $K\alpha$ radiation. Of the 2764 reflections scanned, 1039 were below the threshold of measurement. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to the final residual $R=0·046$. All hydrogen atoms were located from a difference map and were refined isotropically. The acridine ring is not planar, the angle between the planes of the two outer rings being 12·50°. The ring nitrogen atom is hydrogen bonded to the hydroxyl group of another molecule and there is an internal hydrogen bond between the two nitrogen atoms of the side chain.

Experimental

Deep yellow crystals of ICR 449-OH were provided by Drs R. M. Peck, R. K. Preston & H. J. Creech of this Institute (Creech, Preston, Peck, O'Connell & Ames, 1972). The crystal data are summarized in Table 1. A roughly ellipsoidally-shaped crystal, 0·16 × 0·16 × 0·20 mm, was used to collect three-dimensional data on a Syntex automated diffractometer with monochromatic Cu $K\alpha$ radiation and the variable θ–2θ scan technique. Intensities were measured for 2764 reflections. The raw data were corrected for intensity loss, presumably due to radiation damage, by means of a linear plot derived from the change in intensity of the measured standard reflections as a function of time of exposure (17% over 92 hr). Values for $\sigma(F)$ were derived from counting statistics and measured instrumental uncertainties. The formula used was $\sigma(F)=(F/2)\{\sigma^2(I)/I^2+\delta^2\}^{1/2}$ where $\sigma(I)$ is derived from counting statistics alone and δ is the measured instrumental uncertainty. There were 1039 reflections for which the measured intensity, $I_{\rm obs}$, was less than $2·33\sigma(I)$. For these reflections, when $I_{\rm obs} \geq \sigma(I)$, the measured value of $I_{\rm obs}$ was used in computing F and when $I_{\rm obs} < \sigma(I)$, F was computed using the value $0·77\sigma(I)$. The intensity data were converted to structure amplitudes by application of Lorentz and polarization factors and an ellipsoidal absorption correction (Johnson, 1963), and placed on an absolute scale with a Wilson plot.

Structure determination and refinement

The structure was determined by direct methods by means of the program *MULTAN* (Main, Woolfson &

Table 1. *Crystal data for 2-[3-(9-acridinylamino)-propylamino]ethanol*

Empirical formula: $C_{18}N_3OH_{21}$	F.W. 295·4
Crystal system: monoclinic	
$a = 15{\cdot}618$ (2) Å	
$b = 10{\cdot}281$ (1)	$\beta = 102{\cdot}61$ (1)°
$c = 9{\cdot}713$ (1)	
from 15 reflections measured on a diffractometer with Cu $K\alpha$ radiation,	
$\lambda = 1{\cdot}5418$ Å	
$V = 1522{\cdot}0$ (3) Å^3	$F(000) = 632$
$D_x = 1{\cdot}29$ g cm^{-3}	$Z = 4$
$D_m = 1{\cdot}27$ g cm^{-3} (in aqueous KI)	
μ(Cu $K\alpha$) = 6·56 cm^{-1}	
Space group: $P2_1/a$	Systematic absences:
$(\sin\theta/\lambda)_{\max} = 0{\cdot}60$ Å^{-1}	$0k0$, k odd
	$h0l$, h odd

Germain, 1971) using only three-dimensional reflections. All non-hydrogen atoms were located in the E map and the initial trial structure gave a residual $R = 0{\cdot}26$. Two cycles of isotropic block-diagonal least-squares refinement reduced this value to 0·12 and 2 subsequent cycles of full-matrix least-squares anisotropic refinement gave $R = 0{\cdot}09$. The positions of the hydrogen atoms were derived from a difference Fourier synthesis. The structure was then refined anisotropically (hydrogen atoms isotropically) to $R = 0{\cdot}046$ after an extinction correction (Zachariasen, 1963) had been applied with $\alpha = 1{\cdot}3 \times 10^{-6}$.

The atomic scattering factors used for oxygen, nitrogen and carbon atoms were those in *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms those of Stewart, Davidson & Simpson (1965). Computer programs used in this determination were the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970), *UCLALS*4 (full-matrix least-squares program, Gantzel, Sparks, Long & Trueblood, 1969), mod-

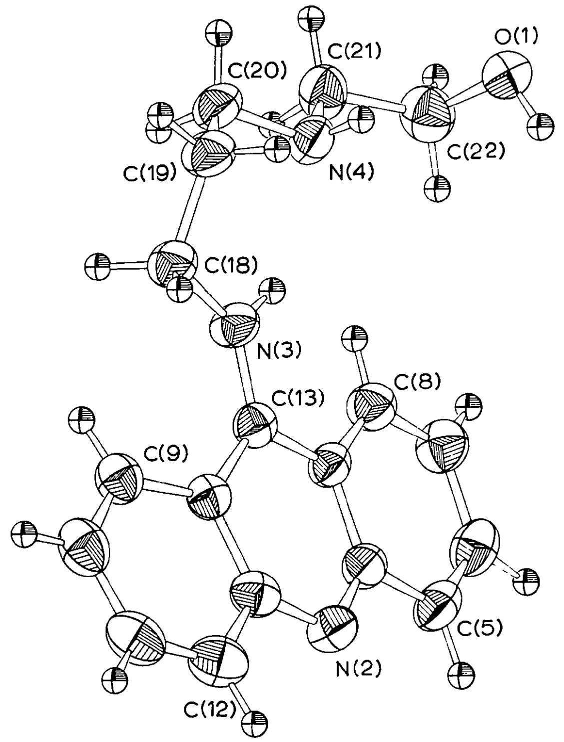


Fig. 1. Thermal ellipsoids for ICR-449-OH drawn with the computer program *ORTEP*.

Table 2. *Final atomic parameters*

Positional parameters are given as fractions of cell edges $\times 10^4$ ($\times 10^3$ for hydrogen atoms). Anisotropic temperature factors are expressed as:

$$\exp\left[-\tfrac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})\right]$$

and isotropic temperature factors as: $\exp(-B\sin^2\theta/\lambda^2)$, with B values given in Å^2. The standard deviations for each parameter, determined from the inverted full matrix, are given in parentheses and apply to the last specified digits.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	3864 (1)	408 (2)	5084 (2)	6·13 (9)	3·31 (8)	3·65 (7)	−0·43 (7)	1·49 (7)	−0·25 (6)
N(2)	5520 (1)	7461 (2)	3214 (2)	3·71 (8)	3·09 (9)	3·80 (9)	0·06 (7)	0·97 (7)	−0·47 (7)
N(3)	5334 (1)	3561 (2)	1884 (2)	3·37 (7)	2·87 (9)	4·09 (9)	−0·01 (7)	1·85 (7)	−0·45 (7)
N(4)	4561 (1)	1206 (2)	2687 (2)	3·67 (8)	3·43 (9)	3·16 (8)	−0·25 (7)	1·16 (7)	−0·66 (7)
C(5)	4266 (2)	7179 (2)	4194 (3)	3·95 (11)	3·62 (11)	3·28 (11)	0·73 (10)	0·63 (9)	−0·83 (9)
C(6)	3606 (2)	6438 (3)	4474 (3)	3·61 (10)	4·73 (13)	3·73 (11)	0·68 (11)	1·19 (10)	−0·74 (11)
C(7)	3500 (2)	5137 (3)	4019 (3)	3·56 (10)	4·08 (13)	4·30 (11)	0·14 (10)	1·51 (10)	−0·25 (11)
C(8)	4063 (2)	4623 (2)	3271 (3)	3·66 (10)	3·27 (11)	3·81 (11)	0·03 (9)	1·18 (9)	−0·14 (10)
C(9)	6433 (1)	5509 (2)	657 (3)	3·35 (10)	3·74 (12)	3·48 (11)	0·08 (9)	0·93 (9)	0·22 (9)
C(10)	7023 (2)	6384 (3)	366 (3)	3·88 (10)	4·96 (14)	4·32 (12)	0·32 (11)	1·66 (10)	0·86 (11)
C(11)	7168 (2)	7559 (3)	1118 (3)	3·81 (11)	4·28 (13)	5·42 (14)	−0·45 (10)	1·32 (11)	1·06 (12)
C(12)	6685 (2)	7865 (3)	2068 (3)	3·59 (11)	3·84 (13)	5·14 (14)	−0·51 (10)	0·69 (11)	0·24 (11)
C(13)	5357 (1)	4847 (2)	2144 (2)	2·73 (9)	2·95 (10)	2·65 (10)	0·13 (8)	0·21 (8)	−0·08 (8)
C(14)	5942 (1)	5752 (2)	1709 (2)	2·69 (9)	2·99 (10)	2·89 (10)	0·16 (9)	0·58 (8)	0·12 (8)
C(15)	6025 (1)	7005 (3)	2352 (3)	2·95 (10)	3·07 (11)	3·53 (11)	0·07 (9)	0·31 (9)	0·23 (9)
C(16)	4864 (1)	6663 (2)	3423 (2)	3·29 (10)	2·98 (10)	2·84 (10)	0·28 (9)	0·50 (9)	−0·11 (8)
C(17)	4757 (1)	5364 (2)	2936 (2)	2·90 (9)	2·84 (10)	2·66 (10)	0·32 (8)	0·59 (8)	−0·27 (8)
C(18)	5916 (2)	2761 (3)	1254 (3)	3·84 (10)	3·22 (11)	4·04 (11)	0·26 (9)	1·65 (10)	−0·25 (9)
C(19)	5908 (2)	1357 (3)	1770 (3)	4·33 (11)	3·12 (11)	4·76 (12)	0·53 (10)	1·90 (11)	−0·34 (11)
C(20)	5004 (2)	756 (2)	1578 (3)	4·55 (11)	3·10 (11)	3·98 (12)	−0·13 (10)	1·82 (11)	−0·80 (10)
C(21)	3705 (2)	603 (3)	2552 (3)	3·95 (11)	4·48 (13)	3·48 (11)	−0·92 (10)	1·09 (10)	−0·37 (10)
C(22)	3325 (2)	891 (3)	3823 (3)	4·10 (12)	4·63 (13)	4·63 (14)	−0·21 (11)	1·51 (12)	0·21 (12)

Table 2 (*cont.*)

	x	y	z	B
H(1)	411 (2)	109 (3)	561 (4)	7·5 (11)
H(3)	494 (2)	312 (3)	226 (3)	4·4 (7)
H(4)	492 (2)	95 (3)	349 (3)	5·6 (7)
H(5)	432 (2)	807 (3)	452 (3)	5·6 (8)
H(6)	319 (2)	688 (3)	501 (3)	4·7 (7)
H(7)	300 (2)	464 (3)	420 (3)	6·5 (9)
H(8)	398 (2)	375 (3)	302 (3)	5·5 (8)
H(9)	633 (2)	475 (3)	12 (3)	4·1 (7)
H(10)	730 (2)	620 (3)	−35 (3)	5·5 (8)
H(11)	764 (2)	810 (3)	99 (3)	5·5 (8)
H(12)	678 (2)	868 (3)	258 (3)	6·5 (8)
H(18)	573 (2)	278 (3)	17 (3)	4·9 (9)
H(18′)	652 (2)	309 (3)	156 (3)	5·0 (7)
H(19)	623 (2)	132 (3)	281 (3)	5·4 (7)
H(19′)	626 (2)	85 (3)	124 (3)	6·4 (8)
H(20)	463 (2)	104 (3)	64 (3)	5·1 (8)
H(20′)	505 (2)	−19 (3)	162 (3)	6·3 (8)
H(21)	330 (2)	101 (3)	171 (3)	6·9 (9)
H(21′)	372 (2)	−35 (3)	241 (3)	4·5 (9)
H(22)	271 (2)	43 (3)	373 (3)	6·6 (7)
H(22′)	320 (2)	185 (3)	390 (3)	5·3 (8)

ified by H. L. Carrell, and a molecular geometry program, *ALLD*, written by H. L. Carrell & A. Caron. The weights used in the least-squares refinement were $1/\sigma^2(F_o)$ and reflections for which $I_{\text{obs}} < 2{\cdot}33\sigma(I)$ were assigned zero weights. The quantity minimized was $\sum\omega||F_o|-|F_c||^2$.

The final atomic parameters are listed in Table 2.* A view of the molecule with thermal ellipsoids is illustrated in Fig. 1 (Johnson, 1965).

Discussion of the structure

This structure determination is part of a comparative study on the conformations and modes of packing of

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* The structure factor tables have been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30125. Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

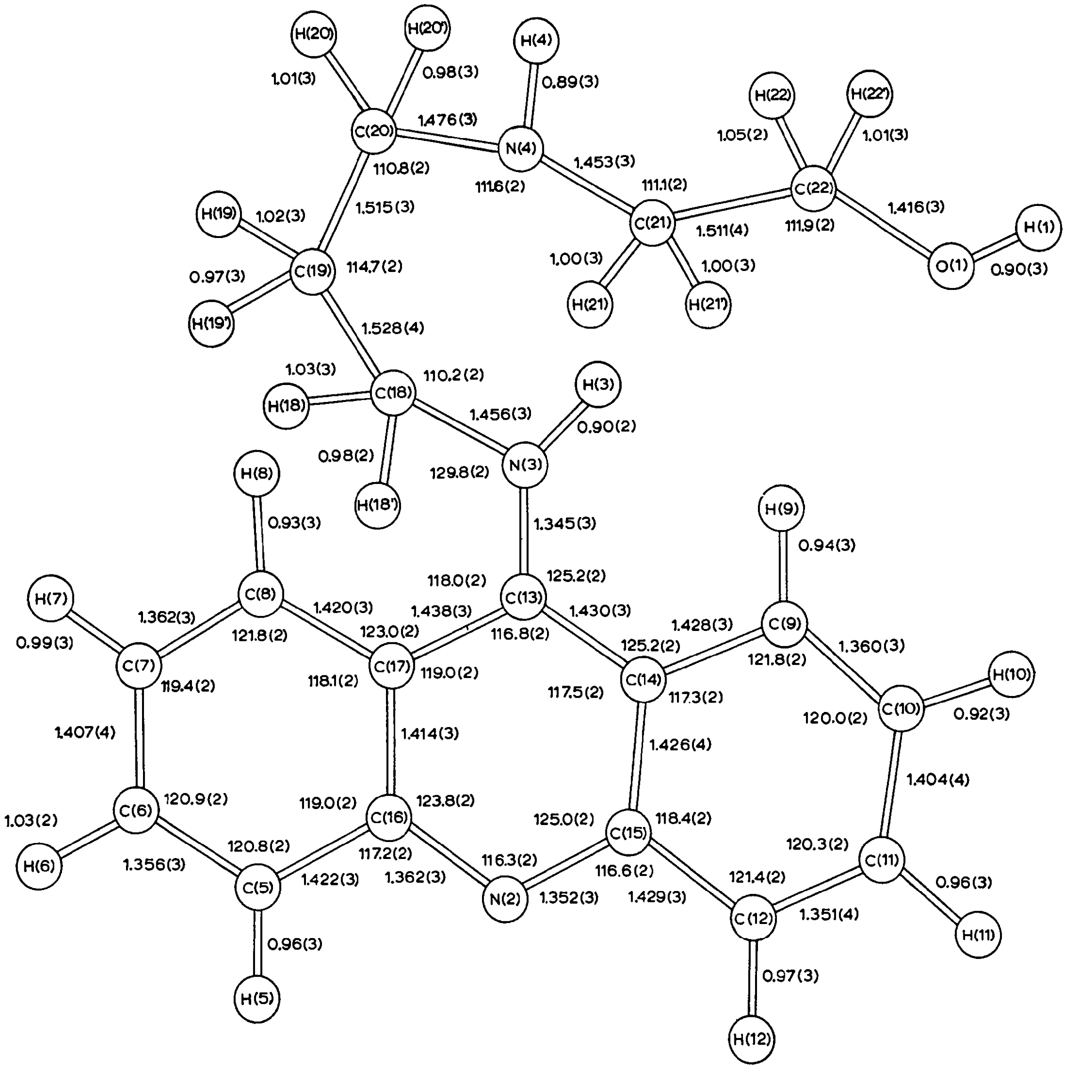
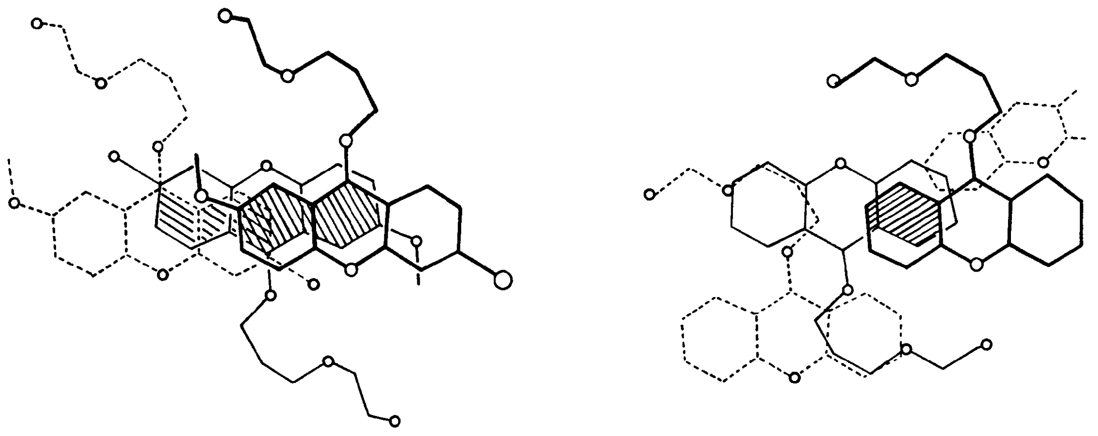


Fig. 2. Angles and distances in ICR-449-OH. Estimated standard deviations are given, in parentheses, with respect to the last digit listed.

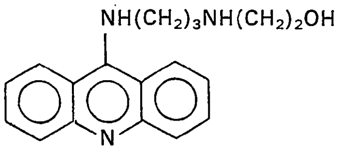


ICR 191 OH

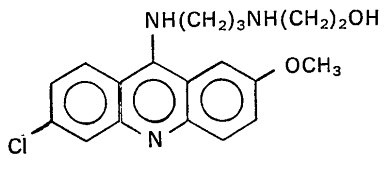
ICR 449 OH

Fig. 3. Overlap of ring systems in ICR-449-OH and ICR-191-OH. Note the different side chain conformations of the two molecules. This diagram is viewed with the acridine system of the main molecules in the plane of the paper. The molecules with ring systems 3·5 Å below the plane of the paper are drawn with broken lines. Oxygen, nitrogen and chlorine atoms are indicated by open circles.

some acridine alkylating agents and their analogues. The nitrogen mustard, ICR-449, is a mutagen for *Salmonella* but not an antitumor agent for ascites tumors. The related compound, ICR-191, with -Cl and -OCH_3 groups substituted in the acridinyl portion of the molecule, is a more powerful mutagen and is also a weak antitumor agent for ascites tumors (Creech *et al.*, 1972). The structure of the hydroxy derivative of ICR-191 (in which the terminal chlorine atom of the alkylating side chain is replaced by a hydroxyl group) has been reported (Carrell, 1972) and will be compared with that of the hydroxy derivative of ICR-449 in this work.

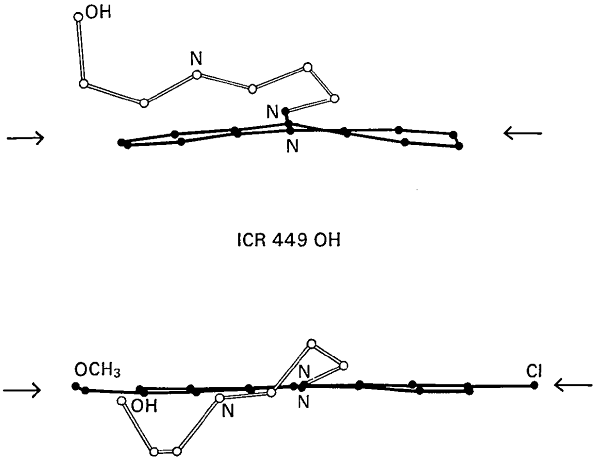


ICR-449-OH
(This work)



ICR-191-OH

The interatomic distances and interbond angles in this molecule are shown in Fig. 2. A comparison of the distances found in this study with those for ICR-191-OH (Carrell, 1972) indicate only minor differences, apart from the effects of the methoxy and chloro substituents of ICR-191-OH on the external angles at these substituted positions in the acridine system. The conformations of the side chains are different, particularly at the ends, as shown in Fig. 3 and Table 3. This difference is seen in the torsion angles C(20)–N(4)–C(21)–C(22) and N(4)–C(21)–C(22)–O(1) which have values



ICR 449 OH

ICR 191 OH

Fig. 4. Views of ICR-449-OH and ICR-191-OH viewed along the best plane through the acridine part of the molecule.

of 170·4 and −60·6° respectively in ICR-449-OH while the comparable torsion angles in ICR-191-OH are 61·3 and 60·2° respectively. The planarities of the two acridine systems are also very different as shown in Fig. 4. The angles between the best planes through the outer rings are 4·9 for ICR-191-OH and 12·5° for ICR-449-OH (4·2 and 8·6° respectively between the best planes of the outer rings with that of the central ring in the latter compound as listed in Table 4). The average r.m.s. deviations from the best plane through the acridine system are 0·125 for ICR-449-OH and 0·047 Å for ICR-191-OH.

Table 3. *Comparison of torsion angles in the side chain*

Torsion angle for atoms	ICR-449-OH	Equivalent atoms in ICR-191-OH
C(13)—N(3)—C(18)–C(19)	153·9	156·1
N(3)—C(18)–C(19)–C(20)	53·0	59·1
C(18)–C(19)–C(20)–N(4)	−78·7	−73·3
C(19)–C(20)–N(4)—C(21)	182·1	169·1
C(20)–N(4)—C(21)–C(22)	170·4	61·3
N(4)—C(21)–C(22)–O(1)	−60·6	60·2

The packing in the crystal is illustrated in Fig. 5 and Table 5 gives the distances and angles involved in the hydrogen bonding. There is an internal hydrogen bond between the two nitrogen atoms of the side chain. The

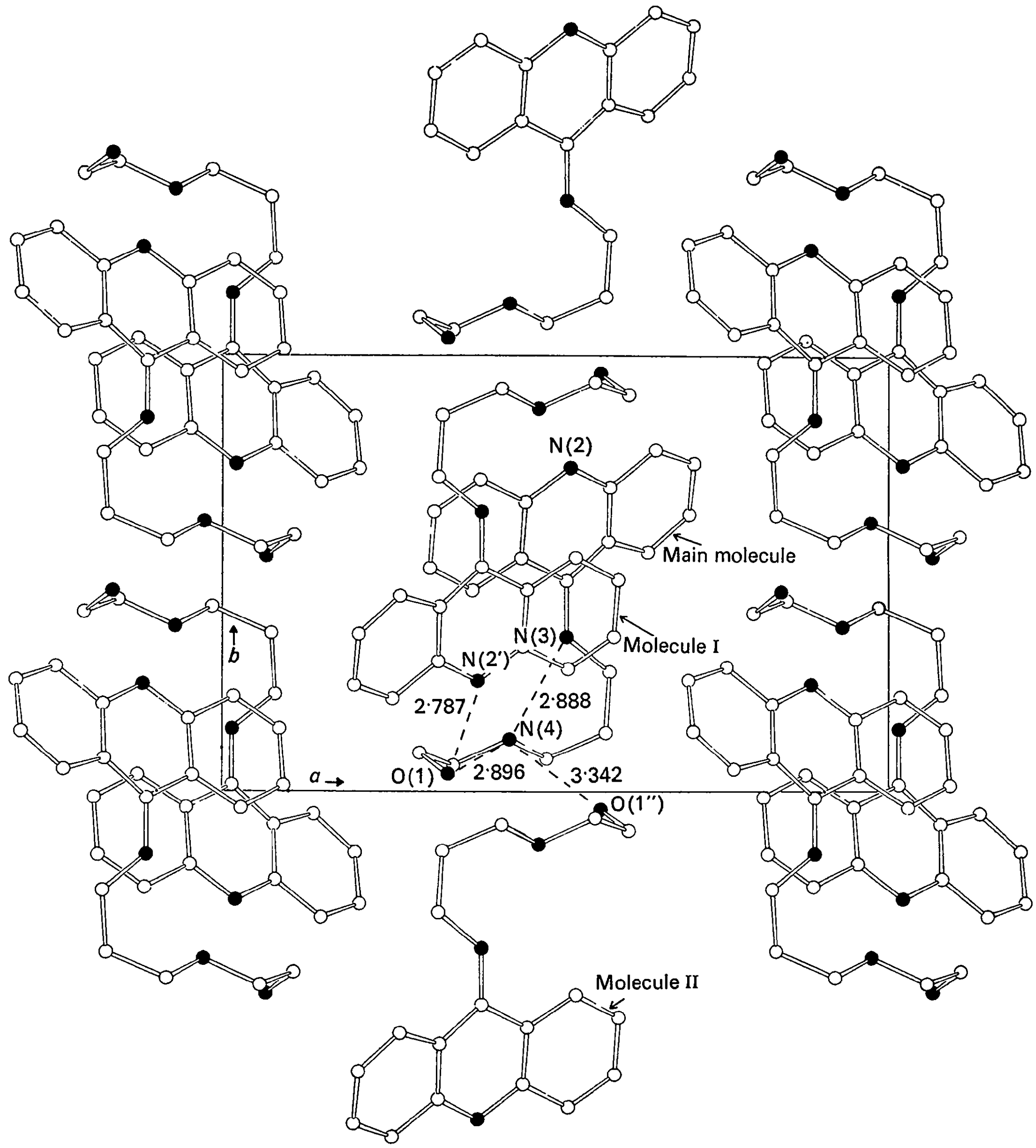


Fig. 5. View, down c*, of the unit-cell contents. Nitrogen and oxygen atoms are black. The molecules referred to in Table 5 are indicated.

Table 4. *Some least-squares planes through parts of the molecule*

An asterisk denotes atoms used to calculate the planes. All deviations from the planes are in Å.

Deviations from the planes

	Plane 1	Plane 2	Plane 3	Plane 4
O(1)	2·489	2·374	2·377	2·577
N(2)	0·043	* 0·050	−0·197	* 0·113
N(3)	0·185	0·310	0·537	0·488
N(4)	0·983	1·038	1·303	1·259
C(5)	* 0·000	−0·153	−0·626	* −0·106
C(6)	* −0·006	−0·222	−0·735	* −0·165
C(7)	* 0·004	−0·176	−0·535	* −0·080
C(8)	* 0·003	−0·078	−0·246	* 0·044
C(9)	−0·574	−0·320	* −0·011	* −0·167
C(10)	−0·664	−0·356	* −0·026	* −0·216
C(11)	−0·396	−0·133	* 0·027	* −0·032
C(12)	−0·131	0·034	* 0·010	* 0·111
C(13)	−0·015	* 0·076	0·161	* 0·218
C(14)	−0·222	* −0·070	* 0·047	* 0·059
C(15)	−0·097	* 0·008	* −0·047	* 0·098
C(16)	* 0·007	* −0·043	−0·317	* 0·032
C(17)	* −0·008	* −0·021	−0·138	* 0·092
C(18)	0·369	0·595	1·029	0·805
C(19)	1·174	1·398	1·905	1·636
C(20)	0·622	0·782	1·257	1·032
C(21)	0·505	0·498	0·731	0·729
C(22)	1·075	0·964	0·991	1·167

Equations of the planes

Plane	
1	$0{\cdot}4257\,X-0{\cdot}3042\,Y+0{\cdot}8522\,Z=3{\cdot}6001$
2	$0{\cdot}4854\,X-0{\cdot}3215\,Y+0{\cdot}8130\,Z=3{\cdot}8150$
3	$0{\cdot}5613\,X-0{\cdot}4101\,Y+0{\cdot}7189\,Z=3{\cdot}6980$
4	$0{\cdot}4903\,X-0{\cdot}3460\,Y+0{\cdot}8000\,Z=3{\cdot}5630$

Where X, Y, and Z are coordinates in orthogonal Ångstrom space with X measured parallel to **a**, Y perpendicular to **a** in the plane of **a** and **b**, and Z perpendicular to the plane of **a** and **b**.

Angles between planes. 1–2 4·21°, 1–3 12·50°, 2–3 8·60° (2 = central ring).

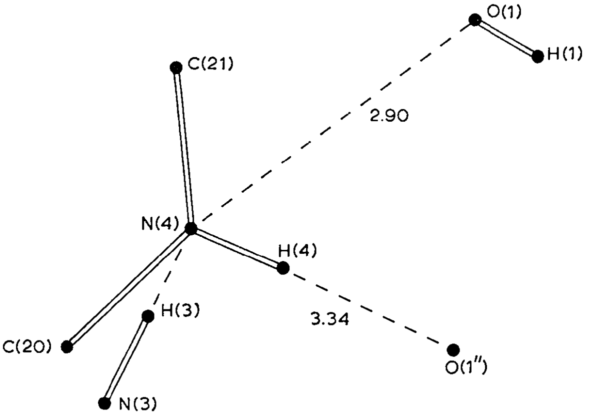


Fig. 6. The surroundings of N(4) and H(4). Distances from N(4) to O(1) and O(1″) are indicated.

ring nitrogen atom of the acridine is hydrogen bonded to the oxygen atom of the hydroxyl group of the side chain of another molecule. As seen in Table 5, the hydrogen atom, H(4), does not form a strong hydrogen bond but is near both O(1) and O(1″). The angular relationships indicate that the N(4)–H(4) bond points towards O(1″), but the interatomic distance indicates that this interaction is weak. This is illustrated in Fig. 6. The shortest carbon–carbon contact distances are given in Table 5(*b*). The molecules pack in pairs across the centers of symmetry. In the side chains the shortest contacts are between C(20) in two molecules that are not hydrogen bonded together.

In the packing of molecules one outer ring of the acridine part of the molecule overlaps that of another molecule as shown in Fig. 3. The part of the alkylating side chain that involves an internal hydrogen bond overlaps the other outer ring of an acridine moiety. It is found, as shown in Fig. 3, from a comparison of overlap of the ring systems in ICR-449-OH and ICR-191-OH, that the effect of substitution in the ring system of ICR-191-OH is to increase both the amount of overlap of rings and the planarity of the acridine moiety.

Table 5. *Packing in the unit cell*

(*a*) Distances (Å) and angles (°) in the hydrogen bond system

D–H···A	A···D	D–H	H···A	D–H···A	H–D···A
O(1)–H(1)···N(2′)	2·787 (3)	0·90 (3)	1·89 (3)	171 (2)	6 (2)
N(3)–H(3)···N(4)	2·888 (3)	0·91 (2)	2·13 (3)	142 (2)	27 (2)
N(4)–H(4)···O(1″)*	3·342 (3)	0·89 (3)	2·52 (3)	154 (2)	20 (2)
N(4)–H(4)···O(1)*	2·896 (3)	0·89 (3)	2·56 (3)	103 (2)	59 (2)

Table 5 (*cont.*)

(*b*) Carbon–carbon intermolecular distances less than 3·6 Å

C(6)—C(12^{v}),	C(12)–C(6^{vi})	3·452 (3) Å
C(6)—C(13^{i}),	C(13)–C(6^{i})	3·583 (3)
C(7)—C(17^{i}),	C(17)–C(7^{i})	3·593 (3)
C(8)—C(16^{i}),	C(16)–C(8^{i})	3·537 (3)
C(9)—C(13)^{iii}),	C(13)–C(9^{iii})	3·469 (3)
C(20)–C(20^{iv})		3·435 (3)

Code for superscripts:

i	$1-x$	$1-y$	$1-z$
ii	$1-x$	$-y$	$1-z$
iii	$1-x$	$1-y$	$-z$
iv	$1-x$	$-y$	$-z$
v	$-x-\frac{1}{2}$	$1\frac{1}{2}-y$	z
vi	$\frac{1}{2}+x$	$1\frac{1}{2}-y$	z

* See text.

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Generalization of Baur's Correlations between Bond Length and Bond Strength in Inorganic Structures

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From results published by Baur it has been possible to show that for a given cation X with a given coordination number, the percentage variation of an X–O bond length from its average value is proportional to the difference between the actual bond strength received by the oxygen and the strength (2 v.u.) which the oxygen should receive according to Pauling's second rule. A correlation between the reduction of X–O length and the increase in X–O–X angle is discussed.

Introduction

Many authors have recently tried to establish empirical relationships between bond lengths and angles in inorganic structures and quantities involved in theoretical models of the chemical bond. Baur (1970), Brown & Shannon (1972, 1973) and Donnay & Allmann (1970) have introduced modifications to Pauling's second rule by correlating bond lengths with bond strengths; Cruickshank (1961), Gibbs, Hamil, Louisnathan, Bartell & Yow (1972) and Louisnathan & Gibbs (1972*a*, *b*, *c*) have related bond lengths and angles directly to the contribution of different electronic orbitals involved in the chemical bond; in addition, Kálmán (1971) has found a linear relationship between X–O average distances and the number *n* of the non-compensated electrons delocalized on the corresponding XO_4^{n-} tetrahedra. We shall be concerned essentially with the first approach.

Pauling's (1929, 1960) statement that 'in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations' is borne out in practice by most ionic structures.* Deviations from this rule are usually interpreted by stating that the electrostatic bond strength *p* received by anions must depend on anion–cation distances.

Within this context, Donnay & Allmann (1970) and Brown & Shannon (1972, 1973) have defined a new bond strength s_i for a given bond X_i–O with length *L*, such that the relation $\sum s_i = 2$ v.u. is still valid. Brown & Shannon (1972, 1973) have found the following empirical equation:

$$s_i = s_{i,0}(L/L_0)^{-N} ; \qquad (1)$$

L_0 and *N* are parameters to be fitted and $s_{i,0}$ is an 'arbitrarily' chosen parameter which, however, has been set very close to Pauling's bond strength p_i; L_0, in its turn, approaches closely the mean value L_m of measured bond lengths *L*. Similar equations have been given by Donnay & Allmann (1970) and by Pyatenko (1973).

Baur (1970, 1971) considered the dependence of the single cation–oxygen distance on the total bond

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* Terms such as 'ionic structure' and 'electrostatic bond strength' will always have a strictly formal meaning, without the claim that a real ionic model is exactly valid.