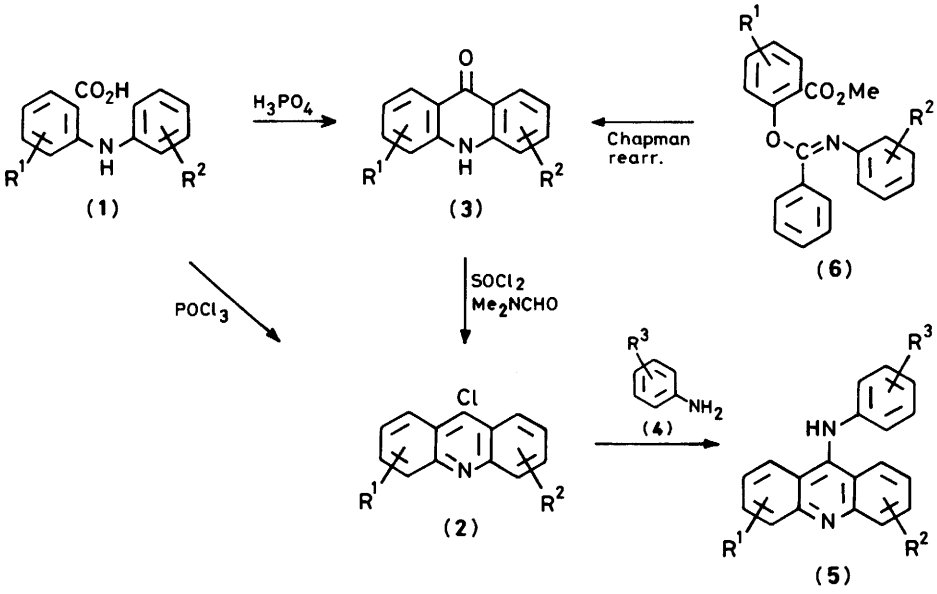
Mechanism of the Chapman Rearrangement of *N*-Arylbenzimidates on the Basis of a Molecular Structure established by *X*-Ray Crystallography

Michio Kimura
Niigata College of Pharmacy, 5829 Kamishin'ei-cho, Niigata, 950-21, Japan

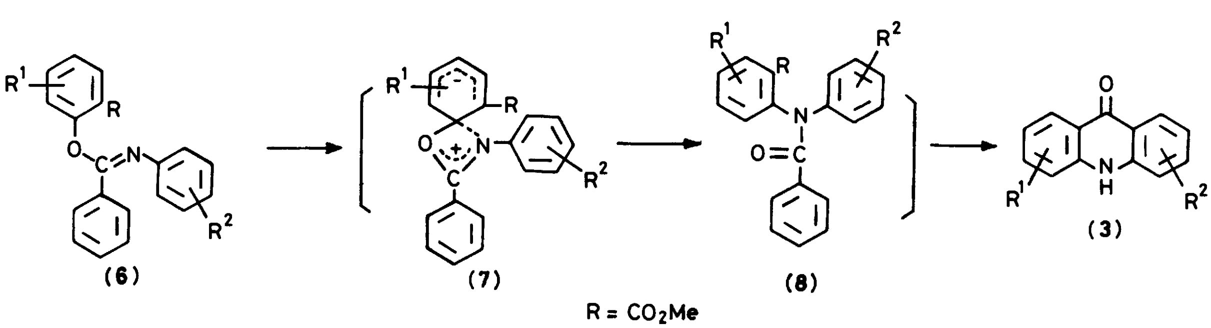
The crystal and molecular structure of 2-methoxycarbonyl-1-naphthyl *N*-(1-naphthyl)benzimidate (**11**), which gives dibenz[*ch*]acridinone (**13**) in the Chapman rearrangement, has been determined by *X*-ray diffraction. The mechanism of the Chapman rearrangement can be interpreted on the basis of the *X*-ray data, in particular the observation of a non-bonded N ••• C interaction (2.648 Å).

The acridines provide a large number of basic dyestuffs, and a useful series of chemotherapeutic drugs which have antibacterial, antimalarial, mutagenic, and carcinogenic properties.[1–6] Recently, a large number of 9-anilinoacridines have been synthesized and tested for antitumour activity.[7–14] Some 9-anilinoacridines, particularly 4′-(acridin-9-ylamino)methanesulphonanilide (AMSA),[15–19] have a broad spectrum action against a number of tumour systems.

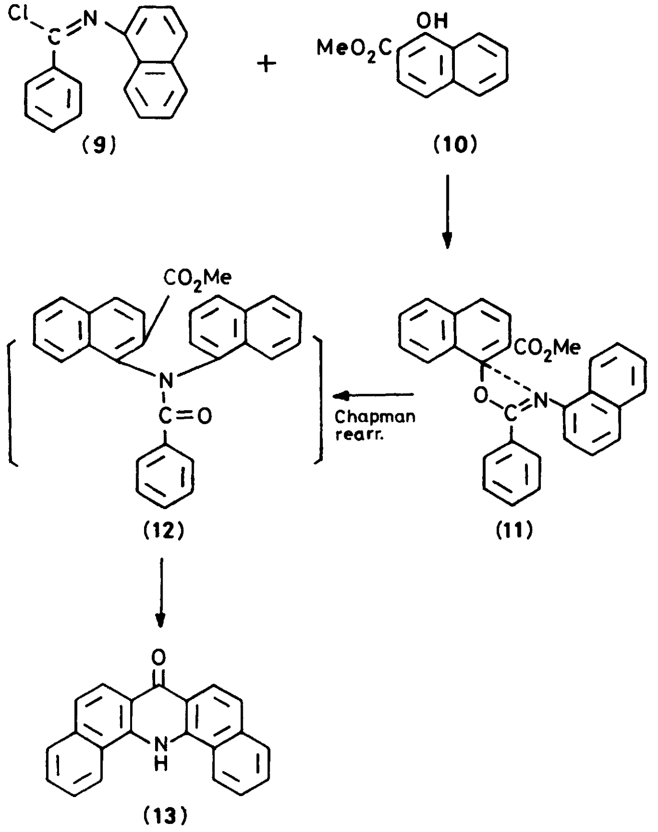
In the preparation of the 9-anilinoacridines (**5**), arylamines (**4**) were coupled with 9-chloroacridines (**2**), obtained directly from the ring closure of an *N*-arylanthranilic acid (**1**) with $POCl_3$.[20–22] When the ring closure with $POCl_3$ was not desirable, this was effected with H_2SO_4, H_3PO_4, polyphosphoric acid, or polyphosphate ester to give the 9(10*H*)-acridones (**3**), which were easily converted into the desired 9-chloroacridines (**2**) with $SOCl_2$–Me_2NCHO.[23] An alternative method of obtaining 9(10*H*)-acridones is the Chapman rearrangement[24,25] of *N*-arylbenzimidates (**6**) (Scheme 1). The Chapman rearrangement has been carried out successfully with many *N*-arylbenzimidates, and yields have generally been high.



Scheme 1.



Scheme 2.



Scheme 3.

With regard to its mechanism, Wiberg and Rowland[24,25] showed that the rearrangement obeys first-order kinetics, indicating an intramolecular nucleophilic aromatic substitution. They also reported that, from comparison of the rate constants for corresponding *ortho*- and *para*-R^1-substituted compounds (**6**) (Scheme 2), the *ortho*-substituent hindered free rotation of the aromatic ring, thereby assisting the formation of the four-membered ring required in the transition state (the *ortho*-substituted compounds reacted more rapidly than the *para*-). Thus three factors (resonance, inductive electron-attraction, and steric acceleration due to hindered rotation) play an important role in the rearrangement. These observations led us to expect the existence of a non-bonded N ••• C interaction in *N*-arylbenzimidates, and we decided to seek evidence for this by *X*-ray methods. As both electron-attracting groups on the aryloxy ring and the steric compressibility of the reactant accelerate the Chapman rearrangement, we chose 2-methoxycarbonyl-1-napthyl *N*-(1-naphthyl)benzimidate (**11**), the precursor of dibenz[*ch*]acridine (**13**) (Scheme 3) for the analysis.

Results and Discussion

The molecular structure (**11**) is presented in Figure 1. Bond lengths and angles are shown in Table 3. The average C–C lengths of the two naphthalene rings *A* and *B* are 1.399 and 1.396 Å, respectively; that of the phenyl ring *C* is 1.390 Å. These and the methoxycarbonyl bond lengths [1.440(5), 1.341(5), and 1.205(5) Å] are normal, and the bond lengths of the two naphthalene rings are exactly equivalent within experimental error. Only the moiety defined by C(1), O(15), C(16), and N(17) differs from normal molecular geometry.

In Table 4 the best least-squares planes are given together with the displacements of the atoms from the planes. The torsion angle between the planes of the two naphthalene rings *A* and *B* is 106.91°; the angles between the phenyl ring *C* and the naphthalene rings *A* and *B* are 70.36 and 110.95°, respectively. The plane composed of C(1), O(15), C(16), and N(17) exhibits torsion angles of 72.95, 73.52, and 38.49° with planes *A*, *B*, and *C*. The accurate molecular conformation of compound (**11**) can be deduced on the basis of the molecular geometry described.

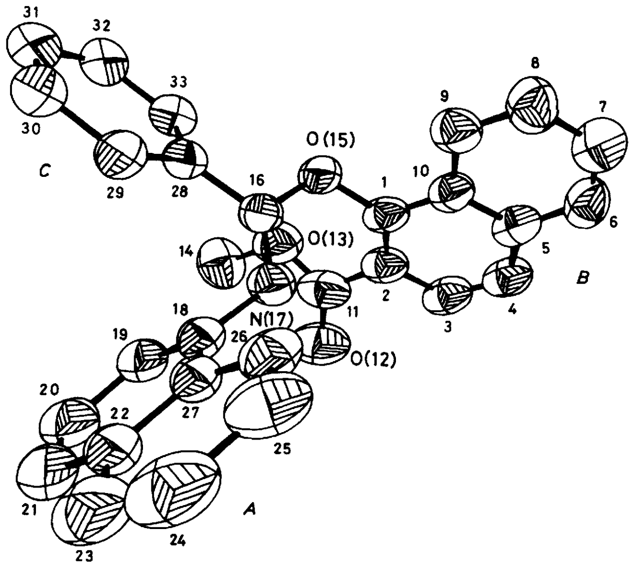


Figure 1. Molecular structure (ORTEP drawing)[37] of (**11**); non-hydrogen atoms are drawn as thermal ellipsoids at the 50% probability level

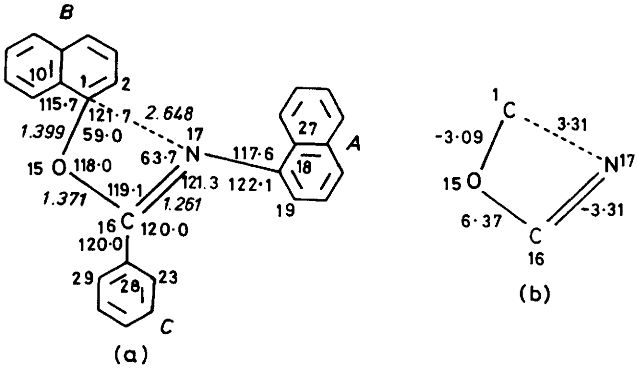


Figure 2. Selected (a) bond lengths and angles, and (b) torsion angles

The Chapman rearrangement has been shown to be an intramolecular reaction in which a 1,3-shift of an aryl group from oxygen to nitrogen takes place. That is, the reaction requires the formation of a four-membered ring in the transition state, and may be considered as a nucleophilic attack by nitrogen on the migrating aryl group. These facts suggest the existence of a non-bonded N ••• C interaction and some bond-angle distortion in the reactant. In fact, there is a non-bonded interaction (2.648 Å) involving N(17) and C(1), much less than the sum of the van der Waals radii (about 3.5 Å).[26] Figure 2 shows the important structural features of compound (**11**) in terms of bond lengths, bond angles, and torsion angles. Other examples are known of unusually short N ••• C distances in molecules containing amino and carbonyl groups; for example 2.910 Å in methadone,[27,28] 2.76 Å in 1-(*p*-methylphenyl)-1-azacyclo-octan-5-one,[29] and 2.76 and 2.69 Å in 1,5-dinitro-3-

methyl-3-azabicyclo[3.3.1]nonan-5-one.[30] The imino linkage (1.261 Å) [C(16)—N(17)] is also significantly shorter than normal values (1.30—1.35 Å).[31] The exocyclic C(1)—O(15) bond is splayed inward and the C(16)—N(17) bond splayed outward; this tends to orient the lone pair more towards the N(17) ··· C(1) direction, readily accommodating the non-bonded N(17) ··· C(1) interaction for the formation of the four-membered ring in the transition state. Thus the thermal conversion of *N*-arylbenzimidates into *N*-arylphenylamines can occur easily.

There are no unusually close intermolecular contacts, the shortest being a carbon–carbon distance of 3.490 Å, greater than the sum of the van der Waals radii. All other intermolecular contacts correspond to normal van der Waals interactions.

Experimental

Compound (**11**) was prepared as described earlier (Scheme 3).[32] The crystals used for the *X*-ray investigation were grown by slow evaporation of a pyridine solution at room temperature. Compound (**11**) had m.p. 142—144 °C (lit.,[32] 141—142 °C); *m/z* 431 (M^+, 100%), 400 ($M^+ - CH_3O$, 15), 372 (8), and 288 (50); $\nu_{max.}$(Nujol) 1 710 and 1 670 cm^{-1}; δ_H (200 MHz; solvent $CDCl_3$; standard Me_4Si) 3.86 (3 H, s, CH_3), and 6.42—8.40 (18 H, m, aromatic); δ_C($CDCl_3$) 52.1, 115.2, 119.5, 122.8, 123.5, 123.7, 125.2, 125.8, 125.9, 126.5, 126.9, 127.4, 127.7, 127.9, 128.2, 128.3, 128.4, 129.5, 130.4, 130.6, 134.0, 136.7, 144.2, 151.2, and 165.7.

Collection and Reduction of Data.—The crystal selected was a cleaved fragment of approximate dimensions 0.20 × 0.25 × 0.30 mm. A preliminary examination with a Rigaku automated four-circle diffractometer showed it to be monoclinic. Systematic absences ($h + k = 2n + 1$, and $l = 2n + 1$ for $h0l$) established the space group as *C*2/*c*. The unit-cell parameters at room temperature were refined by the least-squares method using the Bragg angles [λ(Cu-K_α) 1.541 78 Å] of 24 reflections ($30 < 2\theta < 40$). The unit-cell dimensions and crystal data are listed in Table 1. Intensity data were collected at room temperature with a diffractometer utilizing nickel-filtered Cu-K_α radiation. The θ–2θ scan mode was employed. The scan rate was 4° min^{-1} and the scan range in θ was varied by 1.2° + 0.15° tan θ. Backgrounds were counted for 5 s at both ends of the scan with an offset of 50% of the scan range from the calculated position of the K_α peak. A total of 3 819 unique reflections of the type $h,k,\pm l$ were measured in the range $2\theta < 125°$. The intensities of three standard reflections were measured after every 57 reflections; these intensities dropped by an average of a few percent over the period of data collection, but no correction factor was applied because the decrease was not considered significant. No absorption corrections were applied (μ = 6.24 cm^{-1}). Lorentz and polarization corrections were applied to convert intensities into structure amplitudes. Standard devi-

Table 1. Physical and crystallographic data

Formula unit	$C_{29}H_{21}NO_3$
M	431.50
System	Monoclinic
Space group	*C*2/*c*
Cell constants	
a/Å	19.536(5)
b/Å	13.144(1)
c/Å	17.678(4)
β/°	100.28(2)
V/Å^3	4 466.3
Z	8
D_x/g cm^{-3}	1.283
Instrument	Rigaku AFC diffractometer
Radiation	Cu-K_α
λ/Å	1.541 78
Independent reflections	
Measured	3 819
Observed [$\lvert F_o\rvert > 3\sigma(F_o)$]	2 831
Resolution	MULTAN78[33]
Refinement	UNICS[36]
Final *R*	0.054

Table 2. Final positional and thermal parameters of non-hydrogen and hydrogen atoms with estimated standard deviations

$$B_{eq.} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33})$$

Atoms	*x*	*y*	*z*	$B_{eq.}$ or B/Å^2
C(1)	0.679 1(2)	0.189 6(3)	0.084 8(2)	6.05
C(2)	0.742 8(2)	0.182 6(3)	0.132 2(2)	6.69
C(3)	0.754 3(3)	0.242 4(3)	0.200 7(2)	7.86
C(4)	0.704 5(3)	0.306 4(3)	0.217 5(2)	8.09
C(5)	0.638 9(2)	0.314 3(3)	0.169 9(2)	7.20
C(6)	0.585 1(3)	0.378 6(3)	0.186 4(3)	8.59
C(7)	0.521 9(3)	0.381 3(4)	0.140 1(3)	9.22
C(8)	0.508 4(3)	0.320 4(3)	0.073 3(3)	8.27
C(9)	0.559 0(2)	0.258 0(3)	0.054 6(2)	6.90
C(10)	0.625 5(2)	0.252 4(3)	0.101 7(2)	6.19
C(11)	0.799 7(2)	0.113 9(3)	0.119 9(3)	7.73
O(12)	0.839 4(2)	0.074 2(3)	0.171 5(2)	11.05
O(13)	0.804 8(2)	0.100 9(2)	0.045 9(2)	8.40
C(14)	0.860 3(3)	0.036 1(4)	0.030 7(3)	9.86
O(15)	0.664 4(2)	0.137 1(2)	0.014 9(2)	5.80
C(16)	0.656 9(2)	0.033 5(3)	0.017 3(2)	5.21
N(17)	0.657 2(2)	−0.009 3(2)	0.081 2(2)	6.06
C(18)	0.658 1(2)	−0.117 2(3)	0.088 2(2)	5.59
C(19)	0.713 8(2)	−0.173 5(3)	0.078 5(2)	6.77
C(20)	0.715 8(2)	−0.279 8(3)	0.090 6(2)	7.77
C(21)	0.660 4(3)	−0.327 9(3)	0.112 5(2)	7.66
C(22)	0.601 3(2)	−0.270 9(3)	0.123 5(2)	6.17
C(23)	0.542 8(3)	−0.317 9(3)	0.146 5(3)	8.31
C(24)	0.487 5(2)	−0.262 2(4)	0.158 7(3)	8.83
C(25)	0.487 1(2)	−0.156 2(4)	0.149 9(2)	7.97
C(26)	0.541 6(2)	−0.107 5(3)	0.126 9(2)	6.57
C(27)	0.600 6(2)	−0.164 3(3)	0.113 0(2)	5.41
C(28)	0.647 5(2)	−0.008 8(3)	−0.061 5(2)	5.30
C(29)	0.685 3(2)	0.0311(3)	−0.114 4(2)	6.29
C(30)	0.673 7(2)	−0.006 0(3)	−0.189 8(2)	7.32
C(31)	0.625 5(2)	−0.081 6(3)	−0.211 7(2)	7.37
C(32)	0.588 0(2)	−0.121 0(3)	−0.159 2(2)	7.19
C(33)	0.599 3(2)	−0.085 8(3)	−0.083 4(2)	6.14
H(3)	0.802(2)	0.234(3)	0.236(2)	4.79
H(4)	0.715(2)	0.352(3)	0.268(2)	5.78
H(6)	0.596(2)	0.427(3)	0.232(2)	5.80
H(7)	0.483(2)	0.434(3)	0.153(2)	6.09
H(8)	0.456(2)	0.324(3)	0.033(2)	6.41
H(9)	0.550(2)	0.211(3)	0.004(2)	3.36
H(141)	0.857(2)	−0.037(3)	0.049(2)	5.80
H(142)	0.907(2)	0.070(3)	0.055(3)	7.49
H(143)	0.858(2)	0.036(3)	−0.031(3)	7.64
H(19)	0.758(2)	−0.136(2)	0.060(2)	4.58
H(20)	0.758(2)	−0.319(3)	0.082(2)	5.40
H(21)	0.661(2)	−0.411(3)	0.121(2)	3.66
H(23)	0.545(2)	−0.402(3)	0.153(2)	4.64
H(24)	0.442(2)	−0.297(3)	0.174(3)	6.83
H(25)	0.444(2)	−0.117(3)	0.159(3)	6.50
H(26)	0.544(2)	−0.027(3)	0.117(2)	3.84
H(29)	0.720(2)	0.096(3)	−0.098(2)	3.92
H(30)	0.703(2)	0.024(3)	−0.230(2)	5.06
H(31)	0.616(2)	−0.108(3)	−0.271(2)	4.33
H(32)	0.552(2)	−0.179(3)	−0.174(2)	5.00
H(33)	0.570(2)	−0.116(3)	−0.042(2)	4.38

Table 3. Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(a) Bond lengths for non-hydrogen atoms

C(1)–C(2)	1.375(5)	C(1)–O(10)	1.407(5)	C(1)–C(15)	1.339(3)
C(2)–C(3)	1.429(5)	C(2)–C(11)	1.478(5)	C(3)–C(4)	1.358(5)
C(4)–C(5)	1.406(5)	C(5)–C(6)	1.421(5)	C(5)–C(10)	1.440(4)
C(6)–C(7)	1.355(6)	C(7)–C(8)	1.413(5)	C(8)–C(9)	1.371(5)
C(9)–C(10)	1.415(5)	C(11)–O(12)	1.206(5)	C(11)–O(13)	1.341(4)
O(13)–C(14)	1.441(5)	O(15)–C(16)	1.372(3)	C(16)–N(17)	1.261(4)
C(16)–C(28)	1.482(4)	N(17)–C(18)	1.424(4)	C(18)–C(19)	1.354(5)
C(18)–C(27)	1.418(4)	C(19)–C(20)	1.413(5)	C(20)–C(21)	1.367(5)
C(21)–C(22)	1.419(5)	C(22)–C(23)	1.420(5)	C(22)–C(27)	1.415(4)
C(23)–C(24)	1.354(6)	C(24)–C(25)	1.403(6)	C(25)–C(26)	1.365(5)
C(26)–C(27)	1.431(5)	C(28)–C(29)	1.394(4)	C(28)–C(33)	1.390(4)
C(29)–C(30)	1.399(5)	C(30)–C(31)	1.378(5)	C(31)–C(32)	1.382(5)
C(32)–C(33)	1.397(5)				

(b) Bond angles

O(15)–C(1)–C(10)	115.7(3)	O(15)–C(1)–C(2)	121.7(3)
C(10)–C(1)–C(2)	122.5(3)	C(11)–C(2)–C(3)	116.9(3)
C(11)–C(2)–C(1)	125.1(3)	C(3)–C(2)–C(1)	117.9(3)
C(4)–C(3)–C(2)	121.1(3)	C(5)–C(4)–C(3)	121.8(3)
C(10)–C(5)–C(6)	118.5(3)	C(10)–C(5)–C(4)	118.0(3)
C(6)–C(5)–C(4)	123.4(3)	C(7)–C(6)–C(5)	121.3(3)
C(8)–C(7)–C(6)	120.3(4)	C(9)–C(8)–C(7)	120.5(4)
C(10)–C(9)–C(8)	121.0(3)	C(9)–C(10)–C(5)	118.4(3)
C(9)–C(10)–C(1)	123.0(3)	C(5)–C(10)–C(1)	118.6(3)
O(13)–C(11)–O(12)	122.2(3)	O(13)–C(11)–C(2)	114.2(3)
O(12)–C(11)–C(2)	123.6(3)	C(14)–O(13)–C(11)	116.5(3)
C(16)–O(15)–C(1)	118.0(2)	C(28)–C(16)–N(17)	131.0(3)
C(28)–C(16)–O(15)	109.9(2)	N(17)–C(16)–O(15)	119.1(3)
C(18)–N(17)–C(16)	121.3(3)	C(27)–C(18)–C(19)	120.0(3)
C(27)–C(18)–N(17)	117.6(3)	C(19)–C(18)–N(17)	122.1(3)
C(20)–C(19)–C(18)	121.5(3)	C(21)–C(20)–C(19)	120.0(3)
C(22)–C(21)–C(20)	120.0(3)	C(27)–C(22)–C(23)	118.6(3)
C(27)–C(22)–C(21)	119.6(3)	C(23)–C(22)–C(21)	121.8(3)
C(24)–C(23)–C(22)	121.1(3)	C(25)–C(24)–C(23)	120.6(4)
C(26)–C(25)–C(24)	120.6(3)	C(27)–C(26)–C(25)	120.2(3)
C(26)–C(27)–C(22)	118.9(3)	C(26)–C(27)–C(18)	122.2(3)
C(22)–C(21)–C(20)	118.9(3)	C(33)–C(28)–C(29)	120.1(3)
C(33)–C(28)–C(16)	120.0(3)	C(29)–C(28)–C(16)	119.9(3)
C(30)–C(29)–C(28)	119.5(3)	C(31)–C(30)–C(29)	120.4(3)
C(32)–C(31)–C(30)	119.9(3)	C(33)–C(32)–C(31)	120.6(3)
C(32)–C(33)–C(28)	119.4(3)		

Table 4. Least-squares planes and deviations (Å) of atoms from the planes

Plane A: C(18)—C(27)

$-0.2564X - 0.1270Y - 0.9582Z + 4.5314 = 0$

C(18)	0.031	C(19)	0	C(20)	−0.024
C(21)	−0.015	C(22)	0.013	C(23)	0.020
C(24)	0.011	C(25)	−0.025	C(26)	−0.016
C(27)	0.005				

Plane B: C(1)—C(10)

$-0.4302X - 0.7401Y + 0.5169Z + 6.6524 = 0$

C(1)	−0.023	C(2)	0	C(3)	0.031
C(4)	0	C(5)	−0.017	C(6)	−0.019
C(7)	0.006	C(8)	0.020	C(9)	0.009
C(10)	−0.008				

Plane C: C(28)—C(33)

$-0.6732X + 0.6914Y - 0.2622Z + 8.4502 = 0$

C(28)	0.005	C(29)	0	C(30)	−0.002
C(31)	−0.001	C(32)	0.006	C(33)	−0.008

ations in the intensities [$\sigma(I)$] and in the structure amplitudes [$\sigma(F_o)$] were derived directly from counting statistics.

Solution and Refinement of the Structures.—The structure was solved by direct methods using MULTAN[33] to calculate phases for 300 $|E|$ values greater than 1.68. The E map computed from the phase set with the largest combined figure of merit (3.00) revealed all non-hydrogen atoms except for one carbon atom of the phenyl ring. The subsequent difference Fourier map readily gave the remaining carbon atom. 2 831 Reflections for which $|F_o| > 3\sigma(F_o)$ were used in the full-matrix least-squares refinement of the structure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight calculated as $1/\sigma^2(F_o)$. An initial refinement using individual isotropic temperature factors for the non-hydrogen atoms led to a conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.162. After successive refinement with anisotropic temperature factors ($R = 0.095$), all the hydrogen atoms were readily located from the difference Fourier map. Included in the further refinement were anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. After four cycles of full-matrix least-squares calculation the refinement had converged to a conventional R value of 0.054 and a weighted $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.049 with a quality of fit factor of 2.48 $\{=[\Sigma w(|F_o| - |F_c|)^2/(N_{obs.} - N_{calc.})]^{1/2}\}$. An extinction parameter was refined, because extinction effects were not considered significant. The hydrogen atoms were refined normally; the isotropic thermal parameters ranged from 3.36 to 7.64. The refinement was completed when the largest shift in any parameter among the non-hydrogen atoms was 0.05σ, while the largest shift for the hydrogen atoms was 0.08σ. The final positional and thermal parameters are given in Table 2. The largest peak in the final difference map (0.2 e $Å^{-3}$) was located near the oxygen atom. The atomic scattering factors for O, N, and C were taken from ref. 34; for H, the scattering factors of Stewart, Davidson, and Simpson were used.[35] Mathematical and computational details are given elsewhere.[36]

Acknowledgements

I thank Professor Masao Kakudo, Professor Noritake Yasuoka, and the staff of the Crystallographic Research Center, Institute for Protein Research, Osaka University, for the use of the diffractometer and the ACOS computer.

References

1 H. Mauss and F. Mietzsch, *Klin. Wschr.*, 1933, **12**, 1276.
2 P. E. Thompson, *Am. J. Trop. Med. Hyg.*, 1961, **10**, 335.
3 E. F. Elslager, *J. Med. Pharm. Chem.*, 1962, **5**, 1159.
4 L. S. Lerman, *J. Mol. Biol.*, 1961, **3**, 18.
5 J. W. Drake, 'The Molecular Basis of Mutation,' Holden-Day, San Francisco, 1970, p. 134.
6 B. F. Cain and G. J. Atwell, *Eur. J. Cancer*, 1974, **10**, 539.
7 G. J. Atwell, B. F. Cain, and R. N. Seelye, *J. Med. Chem.*, 1972, **15**, 611.
8 B. F. Cain, G. J. Atwell, and W. A. Denny, *J. Med. Chem.*, 1975, **18**, 1110.
9 B. F. Cain, G. J. Atwell, and W. A. Denny, *J. Med. Chem.*, 1976, **19**, 772.
10 G. J. Atwell, B. F. Cain, and W. A. Denny, *J. Med. Chem.*, 1977, **20**, 1128.
11 W. A. Denny and B. F. Cain, *J. Med. Chem.*, 1978, **21**, 430.
12 W. A. Denny, G. J. Atwell, and B. F. Cain, *J. Med. Chem.*, 1979, **22**, 1453.
13 B. C. Baguley, W. A. Denny, B. F. Cain, and G. J. Atwell, *J. Med. Chem.*, 1981, **24**, 170.
14 B. C. Baguley, W. A. Denny, G. J. Atwell, and B. F. Cain, *J. Med. Chem.*, 1981, **24**, 520.
15 S. S. Legho, G. R. Blumenschein, A. U. Buzdar, G. N. Hortobagyi, and G. P. Bodey, *Cancer Treat. Rep.*, 1979, **63**, 1961.
16 M. J. Waring, *Eur. J. Cancer*, 1976, **12**, 995.
17 W. R. Wilson, *Chem. N. Z.*, 1973, **37**, 148.
18 P. E. Gormley, *Cancer Res.*, 1978, **38**, 1300.
19 N. B. Furlong, *Cancer Res.*, 1978, **38**, 1329.
20 B. F. Cain, G. J. Atwell, and W. A. Denny, *J. Med. Chem.*, 1977, **20**, 987.
21 W. A. Denny, G. J. Atwell, and B. F. Cain, *J. Med. Chem.*, 1977, **20**, 1242.
22 A. Albert, 'The Acridines,' 2nd. edn., Arnold, London, 1966, p. 403.
23 B. F. Cain, R. N. Seelye, and G. J. Atwell, *J. Med. Chem.*, 1974, **17**, 922.
24 K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.*, 1955, **77**, 2205.
25 J. W. Schulenberg and S. Archer, *Org. React.*, 1965, **14**, 1.
26 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.
27 H. B. Burgi, J. D. Dunitz, and E. Shefter, *Cryst. Struct. Commun.*, 1973, **2**, 667.
28 E. Bye, *Acta Chem. Scand., Ser. B*, 1974, **28**, 5.
29 M. Kaftory and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1975, **31**, 2912.
30 M. Kaftory and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 1.
31 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. III, 1974, Table 4.2.4.
32 J. Cymerman-Craig and J. W. Loder, *J. Chem. Soc.*, 1955, 4309.
33 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
34 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. IV, 1974, p. 71.
35 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
36 T. Ashida and Y. Yasuoka, UNICS-Osaka, Computation Center, Osaka University, 1979.
37 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.

Received 4*th April* 1986; *Paper* 6/671