Fig. 1. Tracé de la molécule donné par le programme *PLUTO* (Motherwell & Clegg, 1978) et numérotation des atomes.

Le cycle dioxa-1,3 aza-6 phospha-2 cyclooctane adopte la forme couronne proche de la symétrie C_s; les deux atomes d'hydrogène H'(C6), H(C8) et le groupement B(4)(H,H',H'') sont en position axiale et *cis*; ils sont donc en forte interaction stérique 1,3 diaxiale deux à deux. Cette forte interaction provoque 'l'ouverture' de la conformation couronne par éloignement des atomes de carbone C(6) et C(8); ce mouvement a pour effet de rapprocher l'atome de bore B(4) dans la direction de l'azote N(5) et du carbone C(16): ceci s'observe clairement à l'aide de modèles Dreiding.

L'atome d'azote est plan et la liaison N(5)—C(16) est fortement raccourcie: 1,382 (7) Å [N(5)—C(7) et N(5)—C(9) sont de 1,455 (7) et 1,447 (8) Å respectivement]; ceci indique une hybridation sp^2 de l'atome d'azote et une forte conjugaison du doublet p avec le système π du substituant phényle fixé sur l'azote N(5). L'atome d'azote N(5) présente donc une faible basicité de Lewis.

La distance P(1)—N(5) = 3,293 (5) Å; la somme des rayons de van der Waals pour ces atomes est de 3,40 Å et la liaison P^{IV}—N: 1,8 Å.

Les points que nous venons de souligner nous incitent à conclure qu'il n'existe pas d'interaction transannulaire de Lewis entre azote et phosphore; le rapprochement de ces deux atomes provient des interactions axiales *cis* citées plus haut.

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2-(4-Chloroanilino)-4-oxo-4,5-dihydro-3-furoic Acid Ethyl Ester, $C_{13}H_{12}ClNO_4$

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Abstract. $M_r = 281\cdot69$, monoclinic, $P2_1/c$, $a = 4\cdot508$ (2), $b = 13\cdot547$ (4), $c = 20\cdot784$ (6) Å, $\beta = 97\cdot61$ (4)°, $V = 1258\cdot1$ (5) Å³, $Z = 4$, $D_x = 1\cdot487$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot318$ mm⁻¹, $F(000) = 584$, room temperature, final $R = 0\cdot039$ for 1571 reflections ($F \geq 3\sigma$, $\sin\theta/\lambda \leq 0\cdot56$ Å⁻¹) and 220 refined parameters. The crystal structure consists of flat molecules stacked along (401).

The heterocyclic ring is almost planar; an intramolecular H bridge closes a six-membered ring between the amino and carboxyl groups. Steric hindrance causes the phenyl ring to be turned through 23·9 (2)° out of the plane of the dihydrofuran.

Introduction. The base-catalysed reaction of 4-chloro-acetoacetic ester with both alkyl and aryl isocyanates

yielded cyclocondensation products, which were almost certainly 2-amino-4,5-dihydro-4-furanones instead of the expected 2,4-pyrrolidinediones (Capuano & Fischer, 1976). Chemical behaviour and ^{1}H NMR spectra supported the aminofuran structure. To avoid any ambiguity, we determined the crystal structure of the reaction product with 4-chlorophenyl isocyanate.

Experimental. Transparent needles (m.p. 444 K) with well-developed forms {001}, {011} and {10$\bar{4}$}, recrystallized from benzene. Sample 0·47 × 0·34 × 0·24 mm cut from large needle, mounted with a along spindle axis of paper-tape-controlled four-circle Siemens AED diffractometer; Zr-filtered Mo radiation; lattice constants refined from 20 centred reflections (25·6 ≤ 2θ ≤ 42·6°). 1800 unique data (h, k, l from 0,0,−23 to 5,15,22) measured to (sinθ/λ)$_{max}$ = 0·56 Å^{-1}, ω–2θ scan at 1° min^{-1}, scan width 1° + α$_1$/α$_2$ splitting. Only random variations of three standard reflections (300, 081, 0,3,12). Lp correction, absorption negligible. Structure solved by heavy-atom technique, H atoms from difference Fourier synthesis. Block-diagonal least squares (Bartlett, 1972) minimizing $\Sigma w \Delta^2 = \Sigma w(|F_o| − K|F_c|)^2$, varying one scale factor, coordinates of all atoms, anisotropic vibration tensors for non-H's and isotropic B's for H's. Final R = 0·039, wR = 0·042, S = 0·614 for 1571 observations [$F_o \geq 3\sigma(F_o)$] and 220 variables; all shifts Δp < σ(p). Empirical weighting scheme (Hughes, 1941): w = 1 for F_o < 28 and w = (28/F_o)^2 otherwise, giving roughly constant ⟨wΔ^2⟩ over ranges of |F_o|; three reflections (10$\bar{4}$, 11$\bar{4}$, 12$\bar{4}$) discarded. Scattering factors for neutral atoms from Onken & Fischer (1968); final difference Fourier map featureless ($\Delta\rho$ < 0·1 e Å^{-3}).

Discussion. The molecular structure and atom numbering are displayed in Fig. 1. Atomic coordinates and the molecular geometry are given in Tables 1 and 2.*

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* Lists of structure factors, anisotropic thermal parameters, bond data involving hydrogen and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39763 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
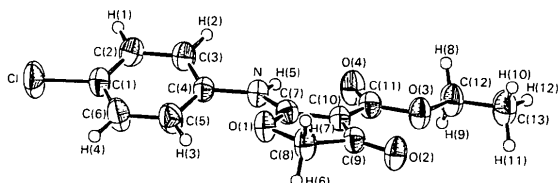

Fig. 1. Perspective view of the molecule and atom numbering. For non-H's the thermal ellipsoids are for 50% probability (Johnson, 1965).

The heterocyclic five-membered ring is almost planar, only atom C(8) being tilted by about 1·8 (4)° out of the plane through atoms O(1), C(7), C(10) and C(9). This geometry is as expected for a delocalized π system extending over the atoms N, C(7), C(10), C(11), O(4), O(1), C(9) and O(2), resulting in bonds of partial double-bond character in accord with the distances actually found.

Table 1. *Fractional atomic coordinates* (×10^4, ×10^3 for H) *and isotropic thermal parameters, with e.s.d.'s in units of the least significant digit in parentheses*

For non-H's the equivalent isotropic temperature factor is defined as: $B = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

	x	y	z	B(Å^2)
Cl	−7502 (2)	2525 (1)	4832 (1)	5·90 (3)
O(1)	1680 (4)	−829 (1)	6499 (1)	3·85 (8)
O(2)	7530 (4)	−1983 (1)	7536 (1)	4·54 (9)
O(3)	8372 (4)	−192 (1)	8322 (1)	3·97 (8)
O(4)	5425 (4)	1079 (1)	7963 (1)	4·69 (9)
N	1279 (4)	746 (1)	6873 (1)	3·36 (9)
C(1)	−5020 (6)	1963 (2)	5439 (1)	3·90 (12)
C(2)	−4616 (6)	2350 (2)	6050 (1)	3·78 (12)
C(3)	−2529 (6)	1922 (2)	6517 (1)	3·63 (12)
C(4)	−940 (6)	1097 (2)	6374 (1)	3·11 (11)
C(5)	−1446 (7)	699 (2)	5758 (1)	4·64 (12)
C(6)	−3490 (7)	1138 (2)	5288 (1)	5·08 (13)
C(7)	2605 (5)	−128 (2)	6932 (1)	3·04 (10)
C(8)	3418 (7)	−1719 (2)	6681 (1)	4·21 (14)
C(9)	5630 (6)	−1423 (2)	7267 (1)	3·39 (11)
C(10)	4930 (5)	−423 (2)	7402 (1)	3·06 (10)
C(11)	6216 (6)	229 (2)	7908 (1)	3·44 (12)
C(12)	9747 (7)	437 (2)	8846 (1)	4·41 (13)
C(13)	11856 (7)	−208 (2)	9273 (1)	5·36 (16)
H(1)	−576 (6)	294 (2)	617 (1)	2·9 (6)
H(2)	−222 (7)	221 (2)	696 (1)	3·2 (7)
H(3)	−38 (7)	11 (2)	568 (1)	4·0 (8)
H(4)	−388 (8)	83 (3)	483 (2)	4·9 (9)
H(5)	202 (7)	120 (3)	718 (2)	4·1 (8)
H(6)	447 (6)	−190 (2)	629 (1)	3·3 (7)
H(7)	201 (7)	−222 (2)	680 (1)	3·8 (7)
H(8)	811 (7)	70 (2)	910 (2)	3·8 (8)
H(9)	1075 (6)	98 (2)	864 (1)	3·2 (7)
H(10)	1083 (7)	−76 (3)	944 (2)	5·2 (8)
H(11)	1344 (7)	−51 (2)	900 (2)	4·8 (8)
H(12)	1285 (8)	22 (3)	962 (2)	5·3 (9)

Table 2. *Intramolecular bond distances* (Å) *and angles* (°) *not involving hydrogen, with e.s.d.'s in parentheses* (*Busing, Martin & Levy,* 1964)

Cl–C(1)	1·747 (3)	O(1)–C(7)	1·336 (3)
O(1)–C(8)	1·459 (3)	O(2)–C(9)	1·223 (3)
O(3)–C(11)	1·337 (3)	O(3)–C(12)	1·455 (3)
O(4)–C(11)	1·215 (3)	N–C(4)	1·424 (3)
N–C(7)	1·325 (3)	C(1)–C(2)	1·363 (4)
C(1)–C(6)	1·371 (4)	C(2)–C(3)	1·386 (4)
C(3)–C(4)	1·381 (4)	C(4)–C(5)	1·379 (4)
C(5)–C(6)	1·385 (4)	C(7)–C(10)	1·393 (3)
C(8)–C(9)	1·523 (4)	C(9)–C(10)	1·426 (3)
C(10)–C(11)	1·437 (3)	C(12)–C(13)	1·494 (4)
C(2)–C(1)–Cl	119·2 (2)	C(6)–C(1)–Cl	118·9 (2)
C(8)–O(1)–C(7)	107·7 (2)	N–C(7)–O(1)	118·5 (2)
C(10)–C(7)–O(1)	114·0 (2)	C(9)–C(8)–O(1)	105·2 (2)
C(8)–C(9)–O(2)	123·2 (2)	C(10)–C(9)–O(2)	131·3 (2)
C(12)–O(3)–C(11)	115·6 (2)	O(4)–C(11)–O(3)	122·8 (2)
C(10)–C(11)–O(3)	113·4 (2)	C(13)–C(12)–O(3)	106·1 (2)
C(10)–C(11)–O(4)	123·8 (2)	C(7)–N–C(4)	129·1 (2)
C(3)–C(4)–N	116·6 (2)	C(5)–C(4)–N	124·0 (2)
C(10)–C(7)–N	127·6 (2)	C(6)–C(1)–C(2)	121·1 (2)
C(3)–C(2)–C(1)	119·1 (3)	C(5)–C(6)–C(1)	119·8 (3)
C(4)–C(3)–C(2)	120·7 (2)	C(5)–C(4)–C(3)	119·3 (2)
C(6)–C(5)–C(4)	119·9 (3)	C(9)–C(10)–C(7)	107·5 (2)
C(11)–C(10)–C(7)	122·0 (2)	C(10)–C(9)–C(8)	105·5 (2)
C(11)–C(10)–C(9)	130·5 (2)		

An intramolecular H bridge between N and O(4) [N⋯O(4) = 2·776 (3),   H(5)⋯O(4) = 2·09 (4) Å] closes a planar six-membered ring comprising N, C(7), C(10), C(11), O(4) and H(5). The ethyl group has a staggered conformation and lies close to the plane of the dihydrofuran [torsion angles: O(4)–C(11)–O(3)–C(12) = –0·5 (4),   C(10)–C(11)–O(3)–C(12) = –179·9 (2), C(11)–O(3)–C(12)–C(13) = 175·0 (2)°].

The phenyl ring itself is planar. The Cl and N atoms, however, show significant deviations of 0·074 (4) and 0·105 (4) Å, respectively, from the mean plane through atoms C(1) to C(6). This seems to be typical for disubstituted benzenes and has been found, for example, in p-chloroaniline (Trotter, Whitlow & Zobel, 1966; Palm, 1966), p-nitrophenol (Coppens & Schmidt, 1965), p-dichlorobenzene (Housty & Clastre, 1957), o-chlorobenzoic acid (Ferguson & Sim, 1961), o-bromobenzoic acid (Ferguson & Sim, 1962) and 2,5-dichloroaniline (Sakurai, Sundaralingam & Jeffrey, 1963).

Repulsion between O(1) and H(3) causes a rotation of the phenyl ring through 23·9 (2)° about the N–C(4) bond away from the plane of the heterocyclic ring [torsion angles: C(7)–N–C(4)–C(5) = –21·3 (4), C(7)–N–C(4)–C(3) = 162·5 (3),   H(5)–N–C(4)–C(3) = –23·2 (2·6)   and   H(5)–N–C(4)–C(5) = 153·0 (2·6)°].

This relatively small torsion, in conjunction with the position of the ester group in the molecular plane, allows a close packing of rather flat molecules parallel to (10$\overline{4}$), largely determined by van der Waals forces.

There are six molecules along the c translation, giving 3·46 Å per molecule, in agreement with the 'thickness' of benzene (3·2 Å) and the space required for Cl (3·5 Å). Each molecule has 12 nearest neighbours; there are no intermolecular contacts closer than expected from the van der Waals radii.

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Methyl [α-(2-Furoyl)benzyl]phenylphosphinate, $C_{19}H_{17}O_4P$

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Abstract. $M_r = 340·31$, orthorhombic, Pbca, a = 18·398 (9),   b = 16·700 (8),   c = 11·034 (6) Å,   V = 3390 (2) Å³, Z = 8, $D_x = 1·33$ Mg m⁻³, Cu Kα, λ = 1·5418 Å, μ = 1·594 mm⁻¹, F(000) = 1424, room temperature, final R = 0·066 for 1008 reflections ($F \geq 3\sigma$, $\sin\theta/\lambda \leq 0·48$ Å⁻¹) and 268 refined parameters. The molecule adopts a staggered conformation. The planes of the two phenyl rings are rotated through 21·7 (8)° with respect to each other. The dihedral angles between the furan, which is planar, and the phenyl rings are 73·2 (8) and 74·7 (8)°, respectively.

Introduction. Photolysis of α-carbonyl-α'-phosphoryl-substituted diazo compounds yields the corresponding carbenes, which normally re-arrange to both ketenes and phosphines (Regitz, 1975). In the case of the 2-furoyl-substituted diazo compounds, however, only the phosphines were observed. These may be stabilized