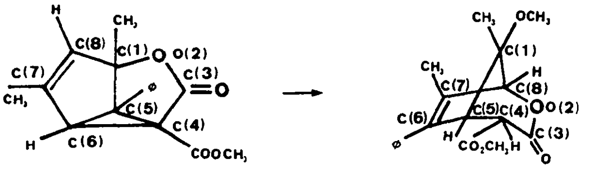

Fig. 2. Schéma de la réaction chimique.

l'axe C(5)—C(8). Pour le cycle hexagonal la liaison C(4)—H(4) est axiale, la liaison C(4)—C(10) est équatoriale. L'angle C(5)—C(1)—C(8) commun aux deux cycles vaut 97,4 (5)°. Cette valeur est beaucoup plus petite que celle attendue (108°). Elle pourrait être due à la répulsion des deux atomes C(9) et O(5). Dans le cycle pentagonal la longueur C(6)—C(7) de 1,350 (5) Å est celle d'une double liaison.

La Fig. 2 montre les transformations opérées lors des réactions chimiques. Il y a eu rupture des liaisons C(1)—O(2) et C(4)—C(6), et formation d'une liaison entre les atomes O(2) et C(8), ce qui entraine le déplacement de la double liaison C(7)—C(8) en C(6)—C(7). Le phényle fixé sur l'atome C(5) se déplace sur l'atome C(6). L'atome d'hydrogène lié a C(6) se fixe soit sur C(4) ou sur C(5). Le méthanol, à chaud, donne un groupement méthoxy qui se lie à C(1) et un atome d'hydrogène qui se placera soit sur C(4) soit sur C(5). La cohésion du cristal est assurée par des liaisons de van der Waals. On peut cependant noter deux contacts directionnels intermoléculaires courts: $H(4^{i})\cdots O(3^{ii})$ 2,35 (6) Å, $C(4^{i})—H(4^{i})\cdots O(3^{ii})$ 154 (7), $C(3^{ii})—O(3^{ii})\cdots H(4^{i})$ 124 (6)°; $H(17^{i})\cdots O(1^{iii})$ 2,47 (6) Å, $C(17^{i})—H(17^{i})\cdots O(1^{iii})$ 94 (7), $C(10^{iii})—O(1^{iii})\cdots H(17^{i})$ 155 (6)° [code de symétrie: (i) *x*, *y*, *z*; (ii) $-x+2, -y, -z+1$; (iii) $-x+1, -y, -z$]. Ces distances sont très inférieures à la somme des rayons de van der Waals (2,70 Å) des atomes d'oxygène et d'hydrogène et pourraient être attribuées à des liaisons hydrogène (Taylor & Kennard, 1982).

Les auteurs remercient Messieurs Valla et Giraud du Laboratoire de Chimie Appliquée aux Corps Organisés du Muséum National d'Histoire Naturelle de nous avoir confié l'étude radiocristallographique de ces trois produits et de nous avoir fourni les cristaux.

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Structure of 2-Acetyl-3-aminobenzofuran

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Abstract. 3-Amino-2-benzofuryl methyl ketone, $C_{10}H_9NO_2$, $M_r = 175\cdot18$, monoclinic, $P2_1/c$, $a = 5\cdot191$ (2), $b = 16\cdot586$ (4), $c = 10\cdot214$ (3) Å, $\beta = 104\cdot00$ (3)°, $V = 853\cdot3$ (5) Å^3, $Z = 4$, $D_x = 1\cdot364$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot9$ cm^{-1}, $F(000) = 368$, $T = 293$ K, $R = 0\cdot056$ for 1391 obser-

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Table 1. *Atomic coordinates and isotropic thermal parameters* (Å²) *with their e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{6}\pi\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0·6695 (4)	0·0783 (1)	0·9648 (2)	0·044 (1)
O(2)	0·1402 (4)	0·1793 (1)	0·7363 (2)	0·049 (1)
C(2)	0·4462 (5)	0·1274 (1)	0·9178 (2)	0·039 (1)
C(3)	0·3688 (5)	0·1648 (1)	1·0225 (2)	0·038 (1)
C(4)	0·5562 (5)	0·1386 (1)	1·1441 (2)	0·038 (1)
C(5)	0·7315 (5)	0·0866 (2)	1·1014 (2)	0·039 (1)
C(6)	0·9407 (5)	0·0488 (2)	1·1893 (3)	0·048 (1)
C(7)	0·9717 (6)	0·0650 (2)	1·3247 (3)	0·051 (1)
C(8)	0·8001 (6)	0·1168 (2)	1·3708 (3)	0·048 (1)
C(9)	0·5909 (5)	0·1537 (2)	1·2816 (3)	0·044 (1)
C(10)	0·3432 (5)	0·1376 (2)	0·7768 (2)	0·040 (1)
C(11)	0·4868 (6)	0·1003 (2)	0·6823 (3)	0·055 (1)
N	0·1615 (3)	0·2161 (1)	1·0115 (2)	0·050 (1)

ved reflections. In the molecule the aminobenzofuran moiety is planar. The N—C and C=O bond lengths are comparable with the dimensions usually found for the amide group. The carbonyl group must be assigned a *syn* configuration with respect to the N atom. Two N···O hydrogen bonds are present.

Introduction. 2-Acetyl-3-aminobenzofuran and its corresponding *N-p*-toluensulfonyl derivatives were allowed to react with hydrazines in order to prepare their related hydrazones as starting materials for the synthesis of compounds with probable psychotropic activity.

The latter compound gave the expected hydrazone in good yield, whereas with the former no reaction was observed. Therefore, we have undertaken an X-ray structural investigation of these compounds in order to understand their different behaviour toward hydrazines. In this paper, the crystal structure of 2-acetyl-3-aminobenzofuran is described; that of the *N-p*-toluenesulfonyl derivative has been reported previously (Bachechi, Coiro, Gatta, Settimj & Delfini, 1988).

Experimental. Crystals were obtained from benzene solution; Nicolet *R*3 four-circle diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; crystal size 0·5 × 0·3 × 0·4 mm; unit-cell dimensions determined from 15 reflections ($20 \leq 2\theta \leq 26°$); 1420 reflections measured in the range $3 \leq 2\theta \leq 56°$, $h = 0$ to 7, $k = 0$ to 23, $l = -14$ to 13; 1391 reflections with $I \geq 3\sigma(I)$ considered observed; ω-scan mode, with scan rate depending on the intensities. Three standards measured every 100 reflections, no significant change; data processed to yield values of I and $\sigma(I)$ (Bachechi, Zambonelli & Marcotrigiano, 1977); in the estimation of $\sigma(I)$ the uncertainty factor was $p = 0{\cdot}0112$, as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections for Lorentz and polarization effects, but not for absorption. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least-squares procedures, function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$ minimized. Heavier atoms with anisotropic thermal parameters; H atoms included at calculated positions with fixed coordinates and isotropic thermal parameters; the contribution of the H atoms of the amino group not considered (109 parameters refined). Convergence at $R = 0{\cdot}056$ ($wR = 0{\cdot}075$, $S = 1{\cdot}28$). $(\Delta/\sigma)_{max} = 0{\cdot}05$; final difference map with no peaks exceeding 0·30 e Å^{-3}. All calculations performed on the HP 2100 MX minicomputer of the CNR Research Area of Rome using local programs (Cerrini & Spagna, 1977). Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters of the non-H atoms are given in Table 1.*

^{1}H NMR spectra were obtained in dimethyl sulfoxide (Me$_2$SO-d_6) and in CDCl$_3$ solutions at room temperature (301 K) on a Bruker WH-90 spectrometer operating at 90·1 MHz in the Fourier transform mode. The concentration of the sample was 5 mg ml^{-1}. The spectral conditions were as follows: spectral width 1200 Hz, 8 K computer memory, pulse width 1·3 μs (30° pulse), number of scans 20. The chemical shifts are reported in p.p.m. from tetramethylsilane (TMS).

^{1}H NMR spectra were also performed at variable temperature (every 5 K) in the range 293–338 K, in Me$_2$SO-d_6 solutions, on an XL-300 Varian instrument operating in Fourier transform mode at 300 MHz. The concentration of the sample was not varied. The spectral conditions were as follows: spectral width 6000 Hz, 16 K computer memory, pulse width 9 μs (45° pulse), repetition time 1·3 s, number of scans 10.

Discussion. Fig. 1 shows the molecular configuration and the atomic numbering and Fig. 2 the crystal packing along the *a* axis. In Table 2 bond lengths and angles are reported. They compare well with those observed in other benzofuran derivatives.

The aminobenzofuran moiety may be considered rigorously planar, no atoms being more than 0·005 Å from the mean plane. N—C(3) and C(2)—C(10) bond lengths are significantly shorter than the expected values for single bonds. The N—C(3) and C=O bond lengths compare with the dimensions usually found for the amide group (Pauling, 1980) and they are indicative of delocalization and involvement in a conjugate system which includes the aminobenzofuran moiety and the C=O group.

Two short N···O non-bonded distances are indicative of two hydrogen bonds: an intramolecular one,

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44836 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

between N and O(2) [2·853 (3) Å] and an intermolecular one between N and O(2) of the molecule at x, $\frac{1}{2}-y$, $z-\frac{1}{2}$ [2·901 (3) Å].

With respect to the *N*-toluenesulfonyl derivative (Bachechi, Coiro, Gatta, Settimj & Delfini, 1988), in which one H atom of the amino group is substituted by a *p*-toluensulfonyl group, the title compound is less planar, the plane through the acetyl group forming an angle of about 8° with the plane of the benzofuran moiety (about 0° in the *N*-toluenesulfonyl derivative).

The N—C(3) bond [1·355 (3) Å] is markedly shorter than in the *N*-toluenesulfonyl analogue [1·406 (4) Å] and this can be regarded as an indication of increasing double-bond character. Consequently, there could be a loss of electrophilicity on C(10) which may be responsible for the lack of reaction with hydrazines in nucleophilic additions.

According to the geometry around the C(2)—C(10) bond the carbonyl group must be assigned the *syn* configuration with respect to the N atom.

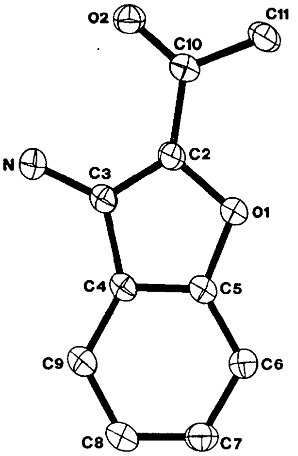

Fig. 1. A perspective view of the molecule. Ellipsoids represent 30% probability.

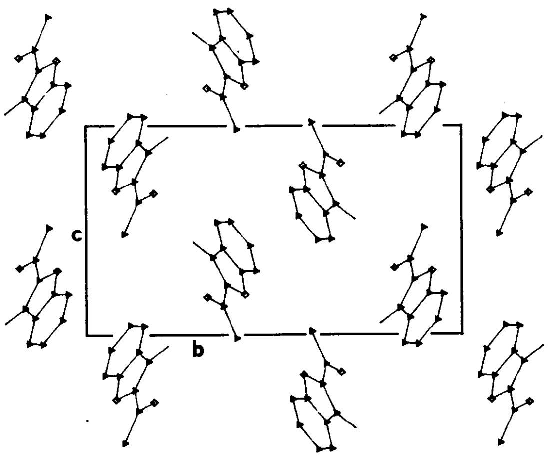

Fig. 2. Crystal packing projected on the *bc* plane.

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

O(1)—C(2)	1·403 (3)	C(4)—C(5)	1·399 (3)
O(1)—C(5)	1·360 (3)	C(4)—C(9)	1·394 (4)
O(2)—C(10)	1·245 (3)	C(5)—C(6)	1·381 (4)
C(2)—C(3)	1·378 (3)	C(6)—C(7)	1·380 (4)
C(2)—C(10)	1·420 (4)	C(7)—C(8)	1·399 (4)
C(3)—C(4)	1·447 (4)	C(8)—C(9)	1·381 (4)
C(3)—N	1·355 (3)	C(10)—C(11)	1·489 (4)

C(2)—O(1)—C(5)	105·3 (2)	O(1)—C(5)—C(4)	111·8 (2)
O(1)—C(2)—C(3)	111·6 (2)	O(1)—C(5)—C(6)	125·1 (2)
O(1)—C(2)—C(10)	119·5 (2)	C(4)—C(5)—C(6)	123·1 (2)
C(3)—C(2)—C(10)	128·7 (2)	C(5)—C(6)—C(7)	116·5 (3)
C(2)—C(3)—C(4)	105·6 (2)	C(6)—C(7)—C(8)	121·9 (3)
C(2)—C(3)—N	126·4 (3)	C(7)—C(8)—C(9)	120·9 (3)
C(4)—C(3)—N	127·0 (2)	C(4)—C(9)—C(8)	118·3 (2)
C(3)—C(4)—C(5)	105·7 (2)	O(2)—C(10)—C(2)	119·0 (2)
C(3)—C(4)—C(9)	135·0 (2)	O(2)—C(10)—C(11)	122·1 (3)
C(5)—C(4)—C(9)	119·3 (3)	C(2)—C(10)—C(11)	118·9 (2)

In solution the ^1H NMR spectrum of 2-acetyl-3-aminobenzofuran shows a signal at δ 2·50 p.p.m. (3 *H*) due to the methyl of the acetyl group and a signal at δ 5·62 p.p.m. (2 *H*) due to the NH group. A complicated multiplet (4 *H*) in the range 7·20–7·70 p.p.m., due to the resonances of the aromatic protons of the benzofuran moiety, is also present.

Another signal, at 1·67 p.p.m., can be attributed to the protons of the acetyl group and amounts to 13% of the total acetyl group signal. Its presence can be considered to result from a second form, in solution, induced by a weak intramolecular hydrogen bond between N and O(2). In this form which corresponds to the *syn* isomer found in the solid state, the hydrogen bond seems to stabilize a spatial arrangement whereby the methyl protons are localized in the anisotropic shielding region of the CO group (Emsley, Feeney & Sutcliffe, 1967).

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