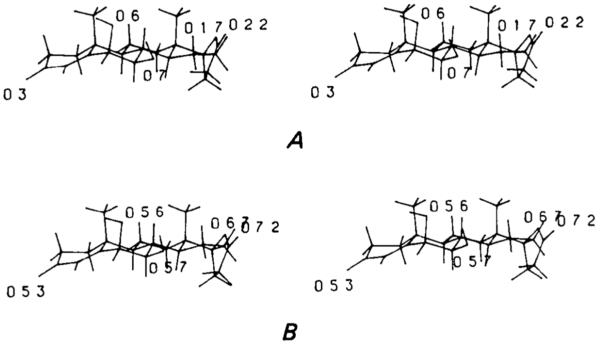

Fig. 1. Vues stéréographiques des molécules *A* et *B*, donnant la numérotation des atomes d'oxygène. Les atomes de carbone sont numérotés suivant la convention habituelle dans les stéroïdes.

L'atome O(6) est en position axiale *β* par rapport au cycle *B*, tandis que O(7) est en position quasi-équatoriale, ce qui explique les difficultés rencontrées lors de l'analyse par RMN: la conformation du cycle *A* est du type enveloppe. Les paramètres de Cremer & Pople (1975) calculés avec le programme *PUCK2* (Luger & Bülow, 1983) sont en effet les suivants: $Q = 0{,}448\ (6)$ Å, $\theta = 52{,}6\ (8)°$ et $\varphi = 18\ (1)°$ (molécule *A*) et $Q = 0{,}447\ (8)$ Å, $\theta = 54{,}6\ (10)°$ et $\varphi = 18\ (1)°$ (molécule *B*). Le cycle *B* est chaise: $Q = 0{,}561\ (6)$ Å, $\theta = 10{,}9\ (6)°$ et $\varphi = 162\ (3)°$ (molécule *A*) et $Q = 0{,}550\ (6)$ Å, $\theta = 13{,}1\ (6)°$ et $\varphi = 187\ (3)°$ (molécule *B*). Le cycle *C* a une conformation similaire: $Q = 0{,}571\ (6)$ Å, $\theta = 9{,}8\ (6)°$ et $\varphi = 266\ (3)°$ (molécule *A*) et $Q = 0{,}547\ (6)$ Å, $\theta = 7{,}3\ (6)°$ et $\varphi = 246\ (5)°$ (molécule *B*). Les cycles *D* et *E* sont intermédiaires entre enveloppe et demi-chaise: *D*: $Q = 0{,}435\ (6)$ Å et $\varphi = 188{,}5\ (8)°$ (molécule *A*) et $Q = 0{,}454\ (6)$ Å et $\varphi = 189{,}1\ (9)°$ (molécule *B*); *E*: $Q = 0{,}262\ (6)$ Å et $\varphi = 26\ (1)°$ (molécule *A*) et $Q = 0{,}256\ (6)$ Å et $\varphi = 33\ (1)°$ (molécule *B*). La cohésion du cristal est assurée par les liaisons de van der Waals et deux liaisons hydrogène: $O(6)[-2-x,\ 0{,}5+y,\ -1{,}5-z]\text{—}O(7) = 2{,}814\ (6)$ Å et $O(56)[0{,}5+x,\ 0{,}5-y,\ -1-z]\text{—}O(57) = 2{,}783\ (6)$ Å.

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Références

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Genard, P. & Palem-Vliers, M. (1981). *Ann. Endocrinol.* **42**, 77.
Genard, P., Palem-Vliers, M. & Eechaute, W. (1977). *Res. Steroids*, **8**, 309–311.
Genard, P., Palem-Vliers, M., Lomba-Pignon, M. R., Christiaens, L. & De Graeve, J. (1985). *Arch. Int. Physiol. Biochim.* Sous presse.
Luger, P. & Bülow, R. (1983). *J. Appl. Cryst.* **16**, 431–432.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et de Louvain-la-Neuve, Belgique.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. de Cambridge, Angleterre.

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1-Bromo-2-naphthaldehyde

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Abstract. $C_{11}H_7BrO$, $M_r = 235{\cdot}09$, triclinic, $P\bar{1}$, $a = 7{\cdot}027\ (3)$, $b = 7{\cdot}430\ (2)$, $c = 9{\cdot}019\ (1)$ Å, $\alpha = 79{\cdot}14\ (2)$, $\beta = 76{\cdot}93\ (2)$, $\gamma = 78{\cdot}32\ (3)°$, $V = 444{\cdot}2\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}758\ (1)$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 45{\cdot}3$ cm^{-1}, $F(000) = 232$, $T = 296$ K, $R(F) = 0{\cdot}032$ for 1508 independent observed reflections. The molecule is planar within experimental error, except for the Br atom, which deviates 0·013 (1) Å from the molecular plane. The aldehyde group is involved in a C—H···Br contact with a H···Br

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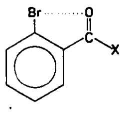
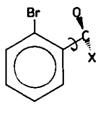
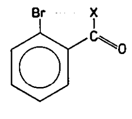
distance of 2·65 (4) Å, but not in any non-bonding C=O···Br interaction. The planar molecules form stacks along **a**.

Introduction. Attractive, non-bonding interactions between hetero atoms have attracted the attention of scientists in various fields of interest. Alcock (1972) has reviewed the crystallographic literature up to 1971. More recently Murray-Rust & Motherwell (1979) have searched the Cambridge Crystallographic Database for structures containing C—X···O intermolecular interactions (X = Cl, Br, I). It has been pointed out by Cody & Murray-Rust (1984) that iodine can form intermolecular interactions of the type C—I···X (X = O, N, S) which play a role in the binding of thyroid hormones to their specific binding proteins. These effects are not just a consequence of crystal packing forces since similar interactions were found in gas-phase *ab initio* calculations (Kollman, Dearing & Kochanski, 1982) and electron diffraction studies (Steines, Shen & Hagen, 1980) of 2-bromo-carbonyl compounds. Possible conformations of *ortho*-bromoaroyl compounds are shown below. In most of these compounds (*i.e.* ketones, carboxylic acids and their derivatives) the residues X are comparable in size or larger than the carbonyl oxygen atom. In this case structures (I) and (II) are preferred according to a search in the Cambridge Crystallographic Database (Koppenhoefer, 1984). We wondered whether the striking preference of conformation (I) over (II) and (III) would be maintained in the sterically less favourable case of aldehyde (X = H). As no structure of this type has yet been published we decided to determine the crystal structure of the title compound.


(I)


(II)


(III)

Experimental. Synthesis as described by Hall & Turner (1955), colourless transparent crystals by recrystallization from methanol/acetone. Crystal dimension 0·17 × 0·22 × 0·70 mm, cell parameters from setting angles of 25 reflections with $15 < \theta < 19°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, sphere up to $2\theta = 50°$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}59$ Å^{-1}, range of hkl ±8, ±8, ±10, ω-scan. Total number of reflections 3120; 1560 independent. Three standard reflections every 5500 s decreased 4%, data rescaling with respect to standards, empirical absorption correction based on ψ scans, correction range 1·0–1·08. Averaging of equivalent reflections, $R_{\rm int} = 0{\cdot}014$. 1508 reflections with $I > 0{\cdot}5\sigma(I)$ used. Weighting scheme $w(I) = [\sigma^2(I) + (0{\cdot}03I)^2]^{-1}$. Structure determination by Patterson and difference Fourier syntheses. All H atoms from difference synthesis, included in refinement with fixed isotropic thermal parameters. Refinement on F, extinction negligible. Final $R = 0{\cdot}032$, $wR = 0{\cdot}034$, $S = 1{\cdot}58$, $(\Delta/\sigma)_{\max} = 0{\cdot}1$. Final difference Fourier map 0·59 e Å^{-3} at Br, but otherwise featureless. Atomic scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Calculations with *SDP* program system (Enraf–Nonius, 1982).

Discussion. The positional parameters are reported in Table 1;* Fig. 1 shows the molecular geometry with the bond lengths and angles. The C—C bond lengths in the

Table 1. *Positional parameters and equivalent values of the anisotropic thermal parameters*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Br	0·36696 (4)	0·29421 (4)	0·24209 (3)	3·924 (6)
O(1)	0·2648 (5)	0·8941 (4)	0·1068 (3)	6·87 (7)
C(1)	0·2889 (3)	0·4728 (4)	0·3796 (3)	2·55 (5)
C(2)	0·2616 (4)	0·6602 (4)	0·3226 (3)	2·99 (6)
C(3)	0·2022 (4)	0·7884 (4)	0·4278 (4)	3·52 (6)
C(4)	0·1732 (4)	0·7313 (4)	0·5811 (3)	3·43 (6)
C(5)	0·2022 (4)	0·5397 (4)	0·6418 (3)	2·67 (5)
C(6)	0·2616 (3)	0·4062 (3)	0·5398 (3)	2·40 (5)
C(7)	0·2888 (4)	0·2154 (4)	0·6037 (3)	3·11 (6)
C(8)	0·2580 (4)	0·1608 (4)	0·7590 (3)	3·69 (7)
C(9)	0·2005 (4)	0·2938 (4)	0·8586 (3)	3·76 (7)
C(10)	0·1735 (4)	0·4776 (4)	0·8016 (3)	3·48 (6)
C(11)	0·2905 (5)	0·7327 (5)	0·1563 (4)	4·49 (7)
H(3)	0·181 (5)	0·898 (4)	0·397 (4)	4
H(4)	0·135 (5)	0·824 (4)	0·641 (4)	4
H(7)	0·329 (4)	0·126 (4)	0·540 (3)	4
H(8)	0·282 (5)	0·023 (4)	0·803 (4)	5
H(9)	0·177 (5)	0·246 (4)	0·967 (4)	5
H(10)	0·135 (5)	0·572 (4)	0·867 (3)	4
H(11)	0·330 (6)	0·634 (5)	0·083 (5)	7

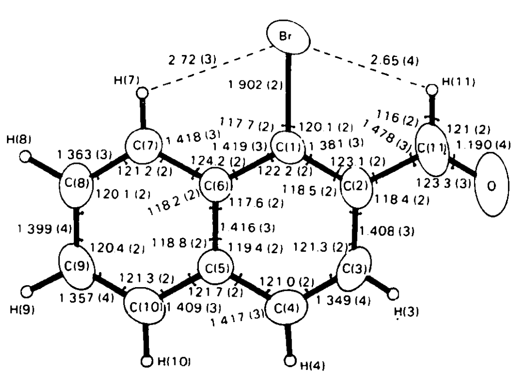


Fig. 1. View of the molecule showing the numbering scheme, bond distances (Å) and bond angles (°).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43105 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

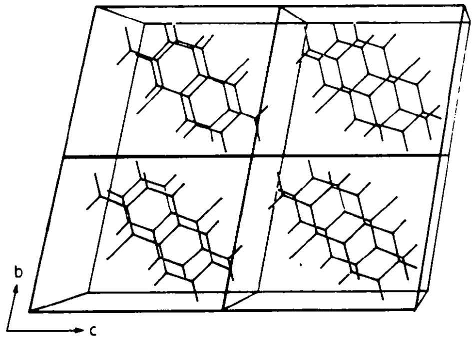

Fig. 2. View of the structure along **a**.

naphthalene molecule are unequal, the C(1)—C(2), C(3)—C(4), C(7)—C(8) and C(9)—C(10) bonds being shorter than all others. Similar bond-length variations have been observed in unsubstituted naphthalene (Cruickshank, 1957; Pawley & Yeats, 1969) and are thus typical for naphthalene. The molecule is planar within the experimental limits except for the Br atom which deviates 0·013 (1) Å from the plane of the other atoms.

The aldehyde group points with its H atom towards the Br atom (conformation III). Thus the dispersion forces between the Br atom and the carbonyl O atom are not sufficient to stabilize conformation (I), which was found for *o*-bromobenzoic acid (Ferguson & Sim, 1962). However, electronic forces may still play a role, as indicated by the preference of the almost planar conformation (III). Stabilization of conformation (III) is achieved by two short intramolecular H···Br contacts: H(11)···Br [2·65 (4)] and H(7)···Br [2·72 (3) Å]. These contacts are considerably shorter than the sum of the van der Waals radii of H and Br (3·15 Å according to Pauling, 1960). The planar molecules form stacks along **a** (Fig. 2). There are no intermolecular contact distances shorter than the sum of the van der Waals radii.

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References

Alcock, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–58.
Cody, V. & Murray-Rust, P. (1984). *J. Mol. Struct.* **112**, 189–199.
Cruickshank, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.
Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft.
Ferguson, G. & Sim, G. A. (1962). *Acta Cryst.* **15**, 346–350.
Hall, D. M. & Turner, E. E. (1955). *J. Chem. Soc.* pp. 1242–1251.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Kollman, P., Dearing, A. & Kochanski, E. (1982). *J. Phys. Chem.* **86**, 1607–1610.
Koppenhoefer, B. (1984). *KSAM. Heidelberger Symposium Struktur-Wirkungs-Beziehungen bei Biomolekülen*, October 1984.
Murray-Rust, P. & Motherwell, W. D. S. (1979). *J. Am. Chem. Soc.* **101**, 4374–4376.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd edition. Ithaca: Cornell Univ. Press.
Pawley, G. S. & Yeats, E. A. (1969). *Acta Cryst.* B**25**, 2009–2013.
Steines, O., Shen, Q. & Hagen, K. (1980). *J. Mol. Struct.* **66**, 181–190.

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Structure d'un dérivé de la Saccharine: le Tribromure de Bis(diéthylamino)-1,3 Diméthyl-2,4 (Trioxo-1,1,3 2*H*-benzothiazol-$1\lambda^6$,3 yl-2)-2 Cyclobuténium. La Géométrie de l'Ion Tribromure

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Abstract. Bromination of a cyclobutenyl saccharinate with *N*-bromosuccinimide in CCl_4–$CHCl_3$ and benzoyl peroxide as catalyst gave the *N*-(cyclobutenyl cation) saccharin tribromide derivative $C_{21}H_{30}N_3O_3S^+.Br_3^-$. M_r = 644·28, monoclinic, $P2_1/c$, $Z = 4$, a = 8·895 (2), b = 15·125 (9), c = 19·985 (9) Å, β = 99·42 (3)°, V = 2652·5 (3·9) $Å^3$, D_m = 1·59, D_x = 1·61 Mg m^{-3}, μ = 46·2 cm^{-1}, Mo $K\bar{\alpha}$ radiation, λ = 0·71069 Å, $F(000)$ = 1288, room temperature, R = 0·035 for 1385 unique diffractometer data. The discrete perhalide counterion is almost linear [Br—Br—Br = 178·53 (7)°] and symmetrical with Br—Br distances of 2·4923 (19) and 2·5625 (19) Å. The organic cation can be viewed as composed of a two-π system, a quasi-planar *N*-