

bond, but even extends to the H positions. The difference between Figs. 3(a) and 3(b), *i.e.* the effect of the 'true' intermolecular interaction (Fig. 3c), would seem to be that the deformation density at the H position is more electron deficient for the short than for the long hydrogen bond, while juxtaposition has the opposite effect (Fig. 3b). The net result is a lower electron density at the H position for the shorter hydrogen bond. This would be further emphasized by O—H bond elongation which occurs in reality, but is not included in the present model calculations.

To summarize, these theoretical calculations show a variation in the electron density at the H nuclear position with respect to hydrogen-bond length. This is consistent with the low electron density found experimentally at the H position in $\text{KH}(\text{HCOO})_2$ ($-0.10 \text{ e } \text{Å}^{-3}$), and with densities observed in other hydrogen-bonded compounds.

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Synthesis and Structures of Tetrahedral Tetrahydrothiophene–Boron Trihalide Adducts, $\text{C}_4\text{H}_8\text{S.BX}_3$ ($X = \text{Cl}, \text{Br}, \text{I}$)

BY BERNT KREBS,* GERALD SCHWETLIK AND MARTIN WIENKENHÖVER

Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, Federal Republic of Germany

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Abstract

Tetrahydrothiophene–boron trichloride, $\text{C}_4\text{H}_8\text{S.BCl}_3$ (I), $M_r = 205.3$, orthorhombic, $P2_12_12_1$, $a = 10.914$ (4), $b = 9.648$ (3), $c = 8.165$ (3) Å, $V = 859.8$ (5) Å³, $Z = 4$, $D_x = 1.59 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) =$

0.71069 Å, $\mu(\text{Mo } K\alpha) = 1.20 \text{ mm}^{-1}$, $F(000) = 433$, $T = 140 \text{ K}$, $R = 0.024$, $wR = 0.030$ for 1076 unique observed reflections [$F > 3.92\sigma(F)$]. Tetrahydrothiophene–boron tribromide, $\text{C}_4\text{H}_8\text{S.BBr}_3$ (II), $M_r = 338.7$, orthorhombic, $Pnma$, $a = 10.696$ (3), $b = 10.182$ (2), $c = 8.695$ (2) Å, $V = 946.9$ (4) Å³, $Z = 4$, $D_x = 2.38 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 13.66 \text{ mm}^{-1}$, $F(000) = 438$, $T = 140 \text{ K}$, $R = 0.044$,

* To whom correspondence should be addressed.

$wR = 0.040$ for 772 unique observed reflections. Tetrahydrothiophene-boron triiodide, $C_4H_8S.BI_3$ (III), $M_r = 479.7$, orthorhombic, $Pbca$, $a = 13.228$ (7), $b = 12.751$ (6), $c = 12.680$ (7) Å, $V = 2139$ (2) Å³, $Z = 8$, $D_x = 2.98$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 8.99$ mm⁻¹, $F(000) = 420$, $T = 140$ K, $R = 0.051$, $wR = 0.041$ for 1461 unique observed reflections. In the molecular Lewis acid-Lewis base adducts, boron is tetrahedrally coordinated by one sulfur and three halogen atoms ($X = Cl, Br, I$), with staggered conformations around the central boron-sulfur bonds. The boron-sulfur bond distances are 1.960 (3) Å in (I), 1.97 (1) Å in (II) and 1.92 (1) Å in (III), indicating that the donor-acceptor B-S bond is strengthened with increasing Lewis acidity of the boron trihalide.

Introduction

A number of novel boron-sulfur compounds with tetrahedral BS_4 coordination have been synthesized recently in our laboratory. They include ternary phases such as $Ag_6B_{10}S_{18}$, $TIBS_2$, $TIBS_3$ and BaB_2S_4 (Krebs & Diercks, 1975, 1984; Krebs, 1983; Krebs & Hamann, 1983, 1984; Eckert, Müller-Warmuth, Hamann & Krebs, 1984; Krebs & Wulff, 1989). Similar tetrahedral coordination around boron can be achieved with mixed halogen/sulfur ligation. The trigonal planar molecular boron trihalides, which are strong Lewis acids because of their unoccupied or partly occupied $2p_z$ orbitals at the B atoms, can be reacted with sulfur-donating Lewis bases such as thioethers (*e.g.* Schmidt & Block, 1970; Morris, Kulevsky, Tamres & Searles, 1966; Brown & Ravindran, 1977; Wienkenhöver, 1985). Tetrahedral BSX_3 ($X = Cl, Br, I$) coordination occurs in which sterically unfavourable crowding is overcompensated by the stabilizing effect of charge donation to electron-deficient boron. It is known that the Lewis acidity of the boron trihalides increases in the order $BF_3 < BCl_3 < BBr_3 < BI_3$ owing to changes in stabilizing effects, such as ion-covalence resonance and ($p-p$) π back-bonding, and as a result of changing repulsion of nonbonding electron pairs. If adducts with Lewis bases such as the presently investigated tetrahydrothiophenes are formed, this trend should result in increasing donor-acceptor bond strength, *i.e.* in decreasing B-S adduct bond lengths in going from BCl_3 to BI_3 . The crystal structures of the adducts with tetrahydrothiophene were studied to search for a possible significant trend in this direction and, in addition, to study conformational effects in the adduct molecules.

Experimental

The microcrystalline 1:1 adducts were prepared by reaction of stoichiometric amounts of the components in nonpolar solvents. Single crystals were obtained by

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) ($\times 10^4$ for Cl, Br, I, S; $\times 10^3$ for C and B) for non-H atoms with *e.s.d.*'s in parentheses

Equivalent isotropic U values are defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
$C_4H_8S.BCl_3$				
Cl(1)	0.41220 (6)	0.22015 (7)	0.20732 (8)	261 (2)
Cl(2)	0.50868 (7)	0.02459 (8)	-0.04988 (9)	364 (3)
Cl(3)	0.53467 (7)	0.33694 (9)	-0.09570 (9)	395 (3)
S	0.69289 (6)	0.18441 (7)	0.14403 (8)	238 (2)
C(1)	0.7154 (3)	0.3491 (3)	0.2497 (4)	30 (1)
C(2)	0.7585 (3)	0.3080 (3)	0.4189 (4)	34 (1)
C(3)	0.6778 (3)	0.1869 (4)	0.4711 (4)	36 (1)
C(4)	0.6768 (3)	0.0835 (3)	0.3316 (4)	31 (1)
B	0.5279 (3)	0.1933 (3)	0.0499 (3)	22 (1)
$C_4H_8S.BBr_3$				
Br(1)	0.60718 (11)	0.250	0.03269 (11)	234 (5)
Br(2)	0.48107 (8)	0.08753 (9)	0.32091 (9)	366 (4)
S	0.3086 (3)	0.250	0.1053 (3)	258 (9)
C(1)	0.3070 (8)	0.1158 (8)	-0.0366 (9)	36 (4)
C(2)*	0.321 (2)	0.192 (2)	-0.201 (2)	45
C(2a)*	0.257 (2)	0.176 (2)	-0.176 (2)	45
B	0.4784 (12)	0.250	0.1921 (13)	22 (5)
$C_4H_8S.BI_3$				
I(1)	0.92107 (7)	0.08105 (7)	0.09225 (8)	340 (4)
I(2)	0.66664 (7)	0.18559 (7)	0.05384 (8)	335 (4)
I(3)	0.74395 (7)	0.07773 (7)	0.31517 (7)	281 (3)
S	0.8210 (3)	0.3010 (2)	0.2171 (3)	231 (9)
C(1)	0.9408 (11)	0.2934 (12)	0.2893 (11)	34 (6)
C(2)	1.0231 (10)	0.3385 (11)	0.2133 (11)	27 (7)
C(3)	0.9689 (11)	0.4191 (10)	0.1463 (13)	38 (6)
C(4)	0.8724 (10)	0.3731 (10)	0.1029 (12)	30 (7)
B	0.7916 (11)	0.1621 (10)	0.1682 (12)	22 (6)

* Occupational factor 0.5; U_{eq} not refined.

sublimation in a temperature gradient. The details of the preparation methods and the spectroscopic data (¹H NMR, ¹¹B NMR in the liquid and solid state, IR, Raman, MS) are reported elsewhere (Krebs, Schwetlik & Wienkenhöver, 1989). Crystals of approximate size 0.4 × 0.2 × 0.4 mm [(I), prisms], 0.01 × 0.10 × 0.13 mm [(II), plates], 0.01 × 0.15 × 0.20 mm [(III), plates], were used to measure the intensities at 140 K of 1112 (I), 1096 (II) and 2350 (III) unique $+h+k+l$ reflections (one octant) in the 2θ range 4–54° on a Syntex P_2 four-circle diffractometer (parallel graphite monochromator, Mo $K\alpha$ radiation, θ - 2θ scan, scan speed in 2θ 5–29.3° min⁻¹, two check reflections). 1076 (I), 772 (II) and 1461 (III) observed reflections with $F > 3.92\sigma(F)$ were used for all calculations. Cell constants were refined from 2θ values of 24 reflections in the range 28–40°. Empirical absorption corrections based on ψ scans were applied; true transmission factors were 0.64–0.74 for (I), 0.22–0.76 for (II) and 0.24–0.83 for (III). The space groups, $P2_12_1$ for (I), $Pnma$ for (II) and $Pbca$ for (III), were derived from systematic absences and intensity statistics.

The structures were solved by direct methods (*MULTAN*) and refined on F by full-matrix least

Table 2. Selected bond lengths (Å) and bond angles (°) involving the non-H atoms with e.s.d.'s in parentheses

C₄H₈S.BCl₃			
B—Cl(1)	1.820 (3)	S—C(4)	1.824 (3)
B—Cl(2)	1.832 (3)	C(1)—C(2)	1.513 (4)
B—Cl(3)	1.828 (3)	C(2)—C(3)	1.524 (5)
B—S	1.960 (3)	C(3)—C(4)	1.514 (4)
S—C(1)	1.825 (3)		
Cl(1)—B—Cl(2)	111.2 (2)	B—S—C(4)	105.3 (4)
Cl(1)—B—Cl(3)	112.3 (2)	C(1)—C(2)—C(3)	106.1 (3)
Cl(2)—B—Cl(3)	112.9 (2)	C(2)—C(3)—C(4)	107.4 (3)
Cl(1)—B—S	111.5 (1)	C(1)—S—C(4)	94.6 (1)
Cl(2)—B—S	103.9 (1)	S—C(1)—C(2)	104.2 (2)
Cl(3)—B—S	104.6 (1)	S—C(3)—C(4)	106.2 (2)
B—S—C(1)	105.7 (1)		
C₄H₈S.BBr₃			
B—Br(1)	1.954 (12)	C(1)—C(2)	1.63 (2)
B—Br(2)	1.998 (6)	C(1)—C(2a)	1.46 (2)
B—S	1.966 (13)	C(2a)—C(2)	1.53 (2)
S—C(1)	1.841 (8)		
Br(1)—B—Br(2)	112.8 (5)	S—C(1)—C(2)	103.5 (7)
Br(2)—B—Br(2)	111.8 (2)	S—C(1)—C(2a)	104.6 (8)
Br(1)—B—S	112.3 (5)	C(1)—S—C(1')	95.9 (4)
Br(2)—B—S	103.2 (5)	C(1)—C(2)—C(2a')	104.8 (12)
B—S—C(1)	105.4 (4)	C(1)—C(2a)—C(2')	108.6 (12)
C₄H₈S.BI₃			
B—I(1)	2.22 (1)	S—C(4)	1.85 (2)
B—I(2)	2.22 (2)	C(1)—C(2)	1.56 (2)
B—I(3)	2.24 (2)	C(2)—C(3)	1.51 (2)
B—S	1.92 (1)	C(3)—C(4)	1.51 (2)
S—C(1)	1.83 (2)		
I(1)—B—I(2)	110.7 (6)	B—S—C(4)	106.4 (6)
I(1)—B—I(3)	110.7 (6)	S—C(1)—C(2)	105.9 (9)
I(2)—B—I(3)	113.5 (6)	S—C(3)—C(4)	102.7 (9)
I(1)—B—S	114.4 (7)	C(1)—C(2)—C(3)	105.4 (11)
I(2)—B—S	103.8 (6)	C(2)—C(3)—C(4)	110.0 (12)
I(3)—B—S	103.4 (6)	C(1)—S—C(4)	95.7 (6)
B—S—C(1)	106.8 (6)		

Symmetry code: (i) $x, \frac{1}{2}-y, z$.

squares with anisotropic temperature factors for all non-H atoms. For (I), the H-atom coordinates were taken from ΔF syntheses and refined; for (II) and (III), the H-atom coordinates were calculated at fixed distances (C—H: 0.95 Å) from the bonded C atoms and included in the structure-factor calculations with $U(\text{H}) = 1.2U(\text{bonded C})$. The weighting scheme was $w^{-1} = \sigma^2(F_o) + cF_o^2$ with $c = 0.0002$ for (I) and (II), and 0.0004 for (III). Scattering factors for neutral atoms (H: bonded atoms) were taken from *International Tables for X-ray Crystallography* (1974). The absolute configuration of (I) in the crystal investigated could not be determined with certainty; after refinement of both enantiomers including anomalous-dispersion corrections the one reported here showed only a marginally better R value (0.030 vs 0.031). A 1:1 split-atom model for two of the tetrahydrothiophene ring C atoms had to be employed for (II) because of disorder across the mirror plane. Attempts to refine the structure in the noncentrosymmetric space group $Pn2_1a$ failed. Minor steric irregularities may also be present at C(3) of (III). The final R values were $R = 0.024$, $wR = 0.030$ for (I),

$R = 0.044$, $wR = 0.040$ for (II), and $R = 0.051$, $wR = 0.041$ for (III). $\Delta/\sigma_{\text{max}} = 0.00$ for (I), 0.01 for (II) and 0.01 for (III). Maximal features in the $\Delta\rho$ maps were below $0.7 \text{ e } \text{Å}^{-3}$ for (I), $1.5 \text{ e } \text{Å}^{-3}$ for (II) and $2.2 \text{ e } \text{Å}^{-3}$ for (III), each close to the halogens. All calculations were performed using the *EXTL* (Syntex) program system and the *SHELXTL* system (Sheldrick, 1981).

Discussion

The atomic parameters with their e.s.d.'s and equivalent isotropic thermal parameters of the asymmetric units are given in Table 1.* Bond lengths and bond angles involving the non-H atoms are shown in Table 2. Figs. 1, 2 and 3 show the structures of the three adduct molecules in the crystal.

In Figs. 4, 5 and 6 the packing of the molecules in the unit cells is given. In all three adducts the B is in fairly regular tetrahedral coordination of one S and three halogen atoms. The B—S bond distances in (I) [1.960 (3) Å] and in (II) [1.966 (13) Å] are longer than in (III) [1.916 (13) Å]. The significant difference between the values for (I) and for (III) indicates that there is a donor–acceptor B—S bond-strengthening effect if the Lewis acidity of the boron trihalide increases. This is in accordance with the data for boron trihalide adducts with dimethylsulfide, dimethylselenide and dimethyltelluride (Krebs, Schwetlik & Wienkenhöver, 1989). It is difficult to interpret the $d(\text{B—S})$ value in (II) within this trend; it is possibly affected by the structural disorder, or by effects of the slightly different conformations in the crystals. The B—S bond lengths in (I), (II) and (III) can be compared with values in the BS_4 tetrahedral building units of $\text{Ag}_6\text{B}_{10}\text{S}_{18}$ (1.915 Å; Krebs & Diercks, 1975, 1984), $\text{Pb}_4\text{B}_4\text{S}_{10}$ (1.927 Å; Krebs, 1983), TlBS_2 and TlBS_3 (1.93 Å; Krebs & Hamann, 1983, 1984), and BaB_2S_4 (1.926 Å; Krebs & Wulff, 1989).

The most significant angular distortions in the SBX_3 ($X = \text{Cl, Br, I}$) tetrahedra of the adduct molecules are the largely increased $X(1)\text{—B—S}$ angles of $111.5 (1)^\circ$ in (I), $112.3 (5)^\circ$ in (II) and $114.4 (7)^\circ$ in (III) (Table 2, Figs. 1, 2 and 3), associated with the B—X bonds closest to the tetrahydrothiophene ligands. They are evidently caused by increasing intramolecular repulsion between $X(1)$ and the five-membered aliphatic ring. Only in the adduct (II), which has m symmetry in its nondisordered part, is a fully staggered conformation around the central B—S bond observed. In (I) the deviation from the staggered form is 9.1° [expressed as

* Lists of structure factors, anisotropic thermal parameters and calculated H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51550 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the angle between a plane bisecting the angle between the Cl(1)–B–S and B–S–C(1)–C(4) planes]. The corresponding torsion angle in (III) is 3.6°. It is suggested that these conformational differences are caused by crystal-packing effects rather than by internal electronic effects. The bond lengths and angles within the puckered aliphatic heterocyclic rings (Table

2) are normal; the C–S bonds are rather long, all angles in the rings are smaller than the tetrahedral ones, the C–S–C angles are especially small, essentially as a result of repulsion with the sulfur lone pairs. In (II) the tetrahydrothiophene ring is disordered across the crystallographic mirror plane (Fig. 2), yielding two equivalent enantiomers in a 1:1 ratio and reducing the

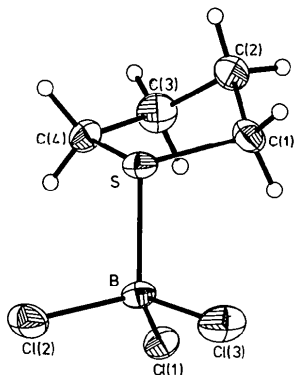


Fig. 1. Molecular structure in the crystal of $C_4H_8S.BCl_3$ (I) with atomic designations and thermal ellipsoids (50% probability level).

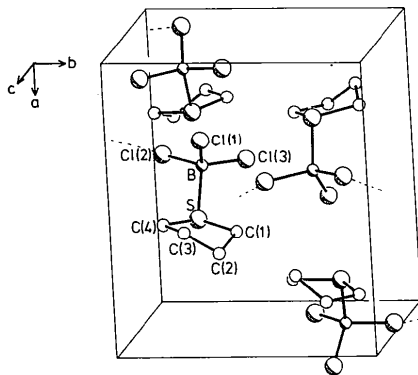


Fig. 4. Packing diagram of (I). Dotted lines: shortest intermolecular Cl...Cl contacts (see text).

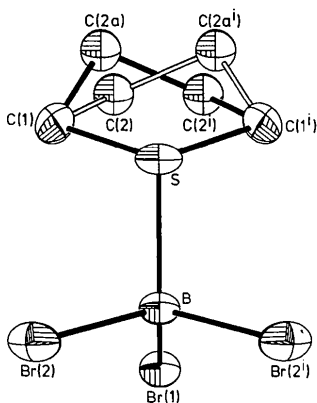


Fig. 2. Thermal ellipsoid plot (50% level) of the disordered molecule of $C_4H_8S.BBr_3$ (II) with atomic numbering.

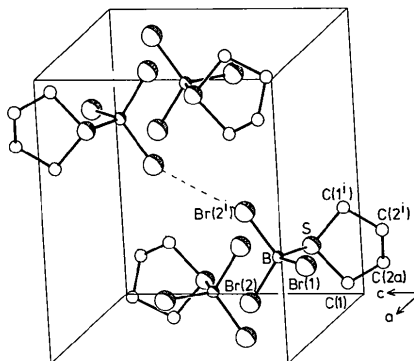


Fig. 5. Projection of the unit cell of (II). Only one of the two halves of the disordered part of the tetrahydrothiophene ring is shown. Dotted lines: as in Fig. 4.

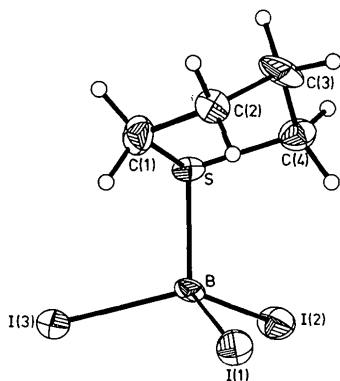


Fig. 3. Molecular structure in the crystal of $C_4H_8S.BI_3$ (III) with 50% thermal ellipsoids and atomic numbering.

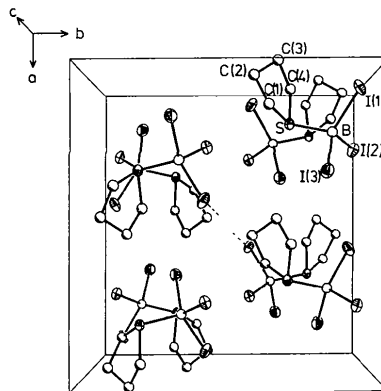


Fig. 6. Molecular packing in the unit cell of (III). Perspective view parallel to *c*. Dotted lines: as in Fig. 4.

precision of the structural results. The packing of the molecules is only slightly influenced by the disorder. All intermolecular contacts are normal. There is one type of short intermolecular halogen...halogen contact in each of the structures with lengths of 3.466 (1) Å for Cl(2)...Cl(3) in (I), 3.611 (1) Å for Br(2)...Br(2) in (II) and 3.756 (1) Å for I(1)...I(1) in (III). The contacts in (II) and (III), which are across centres of inversion, are indicated in the unit cells of Figs. 4, 5 and 6, and may be connected with very weak intermolecular bonding effects.

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What is the Favoured Conformation of the Friedelane Skeleton? A Combined X-ray and Molecular Force-Field Study of Friedelin, C₃₀H₅₀O

BY F. MO, S. WINTHER AND S. N. SCRIMGEOUR*

*Institutt for fysikk, Gruppe for material- og faststoff-fysikk, Universitetet i Trondheim-NTH,
 N-7034 Trondheim, Norway*

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Abstract

Friedelan-3-one, or friedelin has been studied both by X-ray and force-field methods in order to investigate a general conformational problem pertinent to the highly strained *cis*-fused rings *D* and *E* in the friedelane triterpenes. The crystals of friedelin, C₃₀H₅₀O, *M_r* = 426.73, m.p. 535–536 K, are orthorhombic, *P*2₁2₁2₁, *a* = 6.371 (1), *b* = 13.943 (2), *c* = 28.456 (5) Å, *V* = 2527.8 (7) Å³ at *T* = 293 (1) K, *Z* = 4, *D_x* = 1.121 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.060 mm⁻¹, *F*(000) = 952. Diffractometer-data collected from a small crystal specimen contained a very large fraction of weak intensities. Structure solution was by direct methods. Least-squares refinement in the mixed temperature-factor mode was based on 2201 *F_o* and converged at *R* = 0.133. In the crystal structure the *D* ring is a deformed boat and the *E* ring is a boat,

characterizing the stretched conformation. This has been found in eleven of fourteen crystalline derivatives of friedelane and closely related triterpenes. From ball-and-stick models it appears to be the favoured form. Force-field calculations of both the stretched and the folded (= *D* and *E* chairs) forms of the isolated friedelin molecule show that the two are very similar in energy, and the *folded* form is lower in energy by about 3.85 kJ mol⁻¹. One concludes that the conformational preference of a given derivative must be sensitive both to changes in substitution and in the crystalline environment. The calculations allow an analysis to be made of the individual contributions to strain in the two forms. Comparison with previous combined X-ray and force-field studies of similar systems suggests that in the present study of friedelin the calculated structure is more accurate than the experimental one. As part of this work, separate calculations for cyclohexanone have been carried out, and the results compared with those from other calculations and experiments.

* Present address: Department of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland.