

The Disordered Crystal Structure of Bromodifluoroacetamide and Trifluoroacetamide*

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$\text{CBrF}_2\text{CONH}_2$ and CF_3CONH_2 are monoclinic, space group $P2_1/n$, $a = 7.501$ (5), $b = 8.263$ (4), $c = 8.611$ (4) Å, $\beta = 106.19$ (4)°, $Z = 4$, and $a = 6.948$ (7), $b = 7.975$ (3), $c = 7.926$ (7) Å, $\beta = 98.72$ (5)°, $Z = 4$ respectively. The structures have been refined to R_1 indexes of 0.087 and 0.037, respectively, from 523 and 506 independent reflections measured on an X-ray diffractometer. They are isostructural. There is rotational disorder in the series $\text{CXF}_2\text{CONH}_2$ (where $X = \text{F}, \text{Cl}, \text{and Br}$) which appears to decrease with increasing C–X bond length. An electron spin resonance (ESR) single-crystal study supports the presence of disorder in these crystal structures.

Introduction

The crystal structure analyses of $\text{CBrF}_2\text{CONH}_2$ (I) and CF_3CONH_2 (II) were undertaken to aid in the interpretation of ESR experiments on X-ray irradiated single crystals of these compounds. The crystal structure of an analogous compound, $\text{CClF}_2\text{CONH}_2$ (III), previously reported by Kalyanaraman, Kispert & Atwood (1976), showed twofold rotational disorder of the $-\text{CClF}_2$ group about the C–C bond, as shown in Fig. 1. Previous studies on (II) (Small, 1976) also revealed the presence of disorder concerning the $-\text{CF}_3$ group. We have redetermined the structure of CF_3CONH_2 with the same disordered model used for chlorodifluoroacetamide and extended our study to bromodifluoroacetamide, $\text{CBrF}_2\text{CONH}_2$. The results of the electron spin resonance studies for these systems which can be explained on the basis of crystal disorder are also given.

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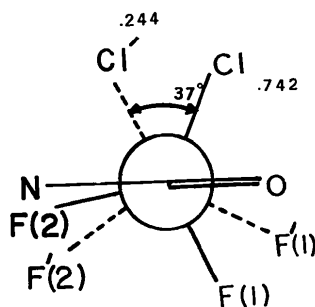


Fig. 1. Projection along the C–C vector showing the observed disorder in chlorodifluoroacetamide. The solid lines represent the location of the major disordered $-\text{CClF}_2$ group.

Experimental

(I) was prepared by the method of Cohn & Bergmann (1964), and recrystallized from ethanol (m.p. $85 \pm 0.5^\circ\text{C}$). A sample checked by gas chromatography was found to be free (<1%) of impurities such as dibromodifluoroacetamide. Analysis: calculated for $\text{CBrF}_2\text{CONH}_2$: C 13.80, H 1.15, N 8.06, Br 45.9, F 21.85%; found: C 13.78, H 1.26, N 8.08, Br 45.77, F 21.72%.

The crystal used for data collection was grown by slow sublimation, ground to a sphere of 0.30 mm diameter and mounted in a thin-walled glass capillary. A CAD-4 diffractometer with graphite-crystal-monochromated Cu radiation, was used to measure the angular settings of 12 reflections from which the cell dimensions were calculated by a least-squares refinement. The crystal data are given in Table 1.

Intensity data for 523 reflections with 2θ less than 140° for the $hkl-\bar{h}kl$ quadrant were collected by the ω -

Table 1. Crystal data for $\text{CBrF}_2\text{CONH}_2$ (I), CF_3CONH_2 (II), and $\text{CClF}_2\text{CONH}_2$ (III)*

	(I)	(II)	(III)*
Formula weight	173.95	113.04	129.49
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	7.501 (5)	6.948 (7)	7.401 (6)
b (Å)	8.263 (4)	7.975 (3)	8.123 (6)
c (Å)	8.611 (4)	7.926 (7)	8.431 (6)
β (°)	106.19 (4)	98.72 (5)	104.48 (5)
V (Å ³)	512.55	434.10	490.76
Z	4	4	4
D_c (g cm ⁻³)	2.254	1.730	1.752
D_m (g cm ⁻³)	2.21	1.78	1.80
$F(000)$	328	224	256
μ (cm ⁻¹)	84.13	2.33	23.40
λ (Å)	1.5418	0.7107	0.7107

* Kalyanaraman, Kispert & Atwood (1976).

2θ scan technique. The method of data collection was standard in the CAD-4 diffractometer, and has been described by Atwood & Sheppard (1975). Two standard reflections were measured after every forty reflections and showed no significant change in intensity during data collection. The intensities were corrected for Lorentz and polarization effects, and a spherical absorption correction was applied (Wehe, Busing & Levy, 1962). No corrections were made for extinction.

The Br position was deduced from a three-dimensional Patterson map, and several structure-factor Fourier-map cycles revealed the positions of all non-hydrogen atoms. The refinement was based on the least-squares minimization of the quantity $\Sigma[w(|F_o| - |F_c|)^2]$ (Busing, Martin & Levy, 1962) with a weighting scheme based on unit weights. Atom scattering factors for Br, F, O, N, and C were taken from Cromer &

Waber (1965); those for H were from *International Tables for X-ray Crystallography* (1962). The scattering for Br was corrected for anomalous dispersion (Cromer & Liberman, 1970).

Refinement with anisotropic thermal parameters for the non-hydrogen atoms gave $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.160$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2} = 0.175$. The thermal parameter of the Br atom was $\beta = 6.29 \text{ \AA}^2$, indicating either high thermal motion or disorder, and rotational disorder similar to that shown in Fig. 1 was suspected. A difference map phased on the positions of C(1), C(2), O and N revealed the locations of two Br atoms with relative peak heights in the ratio 6 : 1.

Table 2. Fractional coordinates for $\text{CBrF}_2\text{CONH}_2$, with e.s.d.'s in parentheses

H atoms are in calculated positions which were not refined. The primed atoms belong to the second conformation.

	Occupancy factor	x	y	z
Br	0.847 (5)	0.3233 (6)	0.3340 (6)	0.2685 (6)
Br'	0.148 (5)	0.218 (4)	0.327 (3)	0.188 (3)
F(1)	0.84 (2)	-0.012 (2)	0.469 (2)	0.272 (2)
F(2)	0.88 (2)	-0.202 (2)	0.484 (1)	0.488 (1)
F(1)'	0.15 (2)	0.038 (14)	0.464 (14)	0.239 (14)
F(2)'	0.16 (2)	0.302 (10)	0.462 (8)	0.457 (8)
O	1.0	0.153 (2)	0.171 (1)	0.557 (1)
N	1.0	-0.099 (2)	0.166 (2)	0.333 (2)
C(1)	1.0	0.128 (2)	0.379 (2)	0.363 (2)
C(2)	1.0	0.061 (2)	0.228 (2)	0.428 (2)
H(1)	1.0	-0.160	0.179	0.241
H(2)	1.0	-0.160	0.107	0.414

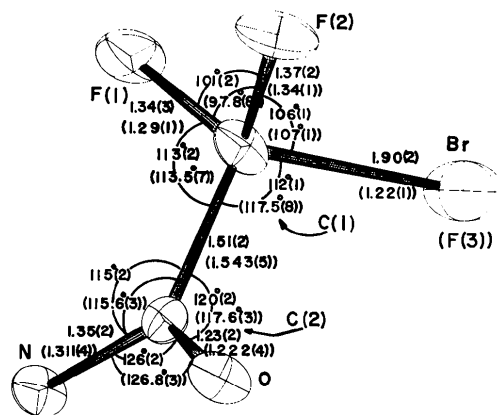


Fig. 2. Molecular structure, atom-numbering scheme, bond lengths (Å) and angles ($^\circ$) for the major disordered conformation of bromodifluoroacetamide, with the atoms represented as their 50% probability ellipsoids for thermal motion. The bond lengths and angles given in parentheses are for trifluoroacetamide. Not shown are the bond angles $\text{Br}-\text{C}(1)-\text{F}(1) = 116(1)^\circ$ and $\text{F}(2)-\text{C}(1)-\text{C}(2) = 110(1)^\circ$ for $\text{CBrF}_2\text{CONH}_2$, and $\text{F}(3)-\text{C}(1)-\text{F}(1) = 111(1)^\circ$ and $\text{F}(2)-\text{C}(1)-\text{C}(2) = 107.4(7)^\circ$ for CF_3CONH_2 .

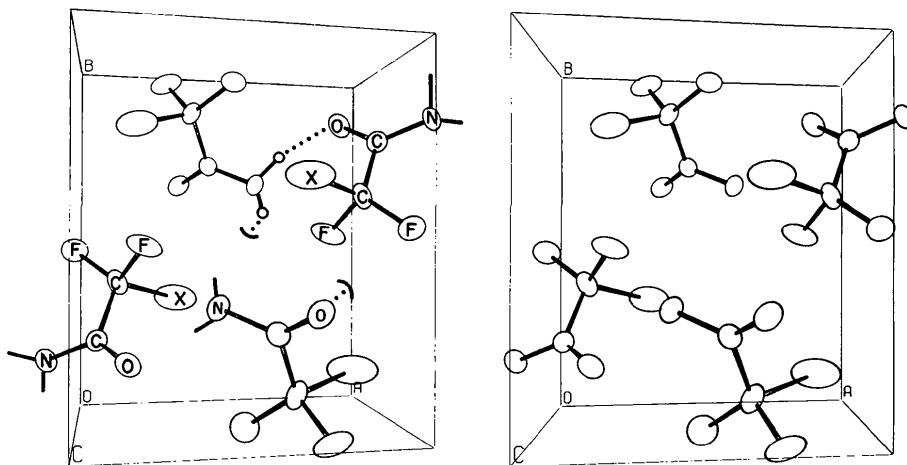


Fig. 3. Packing diagram for bromodifluoroacetamide with $X = \text{Br}$ viewed down the $[001]$ direction (ORTEP, Johnson, 1965).

Least-squares refinement of the disordered model in which the occupancy factor of each disordered atom was varied independently gave $R_1 = 0.087$ and $R_2 = 0.10$.^{*} The largest parameter shifts in the last cycle of refinement were less than 0.10 of their estimated deviations. The height of the largest residual peak was $1 \text{ e } \text{Å}^{-3}$ in the region between the two Br atoms. The atomic coordinates are given in Table 2, the thermal parameters are shown in Table 3, the molecular structure and atom-numbering scheme for the major disordered conformation of bromodifluoroacetamide are given in Fig. 2 and the corresponding packing diagram is shown in Fig. 3.

(II) was obtained from Pierce Chemical Co., and purified twice by sublimation. Single crystals were grown by slowly subliming the purified material.

Lattice constants and intensity data were collected using graphite-crystal-monochromated Mo radiation on a CAD-4 diffractometer. Two standard reflections, 200 and 060, were measured periodically and showed no significant change in intensity during data collection. 506 reflections with 2θ less than 50° were measured.

The structure of trifluoroacetamide, CF_3CONH_2 , was solved directly by *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms resulted in $R_1 = 0.12$ and $R_2 = 0.13$.

Since the thermal factors of all the F atoms were high and the C–F bond lengths short, a further refinement was carried out with a rotational disordered model similar to that depicted in Fig. 1 for $\text{CClF}_2\text{CONH}_2$. Final least-squares refinement of the

^{*} Lists of structure factors for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33066 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Anisotropic thermal parameters for*
 $\text{CBrF}_2\text{CONH}_2$

Anisotropic thermal parameters are $\times 10^3$ in $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All H atoms were assigned an isotropic temperature factor of 5.0 Å^2 . Since the F atoms of lower occupancy in $\text{CBrF}_2\text{CONH}_2$ contribute three electrons to F_c , they were treated isotropically. The isotropic temperature factors of F(1)' and F(2)' were calculated to be 3.09 and 2.73 Å^2 respectively.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	37 (1)	13.0 (5)	35 (1)	-2.6 (8)	25.1 (9)	-1.8 (8)
Br'	37 (7)	12 (3)	23 (5)	-8 (5)	22 (4)	-6 (3)
F(1)	20 (4)	10 (2)	20 (4)	0 (2)	2 (3)	9 (2)
F(2)	25 (3)	8 (2)	13 (2)	-7 (2)	5 (2)	-5 (2)
O	20 (3)	9 (2)	7 (2)	-4 (2)	-10 (2)	2 (2)
N	16 (3)	6 (2)	7 (2)	-5 (2)	-6 (2)	1 (2)
C(1)	15 (4)	8 (3)	9 (3)	0 (3)	0 (3)	-2 (2)
C(2)	21 (4)	7 (2)	9 (3)	0 (3)	6 (3)	-3 (2)

Table 4. *Fractional coordinates for* CF_3CONH_2 , *with e.s.d.'s in parentheses*

H atoms are in calculated positions which were not refined.

	Occupancy factor	x	y	z
F(1)	0.501 (5)	0.221 (2)	0.498 (1)	0.447 (2)
F(2)	0.505 (4)	0.343 (2)	0.345 (2)	0.299 (2)
F(3)	0.504 (5)	0.073 (2)	0.443 (2)	0.207 (2)
F(1)'	0.499 (6)	0.275 (2)	0.462 (2)	0.446 (2)
F(2)'	0.502 (5)	0.229 (3)	0.346 (2)	0.196 (2)
F(3)'	0.501 (4)	0.020 (2)	0.490 (1)	0.282 (2)
O	1.0	0.1775 (3)	0.1669 (3)	0.5417 (3)
N	1.0	-0.0777 (4)	0.1671 (3)	0.3265 (3)
C(1)	1.0	0.1672 (8)	0.3835 (5)	0.3357 (6)
C(2)	1.0	0.0850 (5)	0.2255 (3)	0.4115 (4)
H(1)	1.0	-0.1400	0.2188	1.2187
H(2)	1.0	-0.1400	0.0625	1.3750

Table 5. *Anisotropic thermal parameters for*
 CF_3CONH_2

Anisotropic thermal parameters are $\times 10^3$ in $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All H atoms were assigned an isotropic temperature factor of 5.0 Å^2 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(1)	80 (5)	12.0 (8)	45 (3)	-9 (2)	19 (3)	-6 (1)
F(2)	63 (4)	33 (2)	70 (4)	-18 (3)	41 (3)	-6 (3)
F(3)	105 (9)	60 (5)	47 (4)	-53 (5)	-31 (4)	34 (4)
F(1)'	85 (5)	39 (3)	57 (4)	-43 (3)	-44 (4)	24 (3)
F(2)'	136 (10)	29 (2)	54 (4)	1 (4)	63 (5)	8 (2)
F(3)'	49 (2)	14.4 (9)	50 (3)	4 (1)	-4 (2)	16 (1)
O	32.8 (7)	15.2 (4)	20.3 (4)	-3.0 (4)	-6.0 (5)	1.6 (4)
N	30.9 (8)	15.1 (5)	19.2 (5)	-3.7 (5)	-4.9 (6)	2.7 (4)
C(1)	42 (2)	19.2 (8)	23.9 (9)	-6 (1)	2 (1)	3.1 (8)
C(2)	23 (1)	11.5 (4)	18.9 (6)	-0.7 (6)	3.6 (7)	-1.4 (5)

disordered model gave $R_1 = 0.037$ and $R_2 = 0.035$. The largest parameter shifts in the last cycle of refinement were less than 0.10 of their estimated standard deviations. A final difference Fourier synthesis indicated no electron density greater than $0.3 \text{ e } \text{Å}^{-3}$. The crystal data are given in Table 1, the atomic coordinates are given in Table 4 and thermal parameters in Table 5.

Description of the structures

The interatomic distances and bond angles for the major component of bromodifluoroacetamide and trifluoroacetamide are given in Fig. 2. In the minor component of (I), 14.8% of the CBrF_2 groups are rotated -28° about the C–C bond from that of the major component. The rotational disorder in (II) is greater; 50% of the CF_3 groups are rotated by an average angle of -35° . In (III), 24% of the CClF_2

groups were rotated by an angle of -37° from the remaining CClF_2 groups.

The dihedral angles which the $\text{C}(1)\text{--C}(2)\text{--O}$ (CCO) plane makes with the $X\text{--C}(1)\text{--C}(2)$ plane for the different conformations in this series are given in Table 6. An important difference is noted between the unprimed conformation of (II) and both conformations of (I) and (III). The dihedral angle $\text{F}(3)\text{--C}(1)\text{--C}(2)\text{--O}$ is 180° , placing F(3) in the CCO plane while no F lies in the CCO plane for the prime conformation as the $\text{F}(3')\text{--C}(1)\text{--C}(2)\text{--O}$ dihedral angle is 139.2° . The absence of F atoms positioned coplanar with CCO also occurs for (III) and (I) as the $\text{Cl}\text{--C}(1)\text{--C}(2)\text{--O}$, $\text{Cl}'\text{--C}(1)\text{--C}(2)\text{--O}$, $\text{Br}\text{--C}(1)\text{--C}(2)\text{--O}$ and $\text{Br}'\text{--C}(1)\text{--C}(2)\text{--O}$ dihedral angles are -75.6 , -115.8 , -77.6 and -107° . This conformational difference will be further demonstrated by some ESR results of irradiated (II) and (III).

The hydrogen-bonding is shown in Fig. 3 and the distances are given in Table 7. The shorter intermolecular $\text{H}\cdots\text{F}$ distances are 2.32 and 2.44 Å in (III), 2.34 and 2.44 Å in (II) and 2.53 and 2.63 Å in (I). The shortest $\text{H}\cdots\text{F}$ distance occurs for the F atom which comes nearest to being coplanar with CON [F(3) for CF_3CONH_2 and F(2) for $\text{CClF}_2\text{CONH}_2$]. The

hydrogen-bonded distances and angles (Table 7) fall into the general pattern found in primary amide structures where packing of centrosymmetric related molecules occurs (Hughes & Small, 1972).

Evidence of disorder by ESR measurement

Evidence for rotational disorder is provided by examining the ESR spectra of irradiated trifluoroacetamide, chlorodifluoroacetamide and bromodifluoroacetamide. In general, radicals formed in irradiated crystals retain the spatial arrangement of the parent molecule (Whiffen, 1961). Such radicals formed in monoclinic crystals are located in two magnetically nonequivalent sites in the a^*b and bc planes, while along the a^* , b , and c axes, only one magnetic site is observed.

If disorder occurs, then multiple magnetic sites occur along the a^* , b or c axes owing to the magnetic non-equivalence of the disordered sites.

Such an effect has been observed for irradiated chlorodifluoroacetamide crystals. The ESR spectrum obtained at 90 K for a crystal of 77 K irradiated chlorodifluoroacetamide when the magnetic field is parallel to the a^* axis is given in Fig. 4.† Lines *A* and *B* represent the high- and low-field ESR lines of the four-line spectra which occur for the two magnetically nonequivalent crystal sites of $\cdot\text{CF}_2\text{CONH}_2$. The separation, $A - B$, cannot be due to a hyperfine coupling as the separation between the low-field lines ($A - B = 9.0$ G)

Table 6. Dihedral angles between the $\text{C}(1)\text{--C}(2)\text{--O}$ and $X\text{--C}(1)\text{--C}(2)$ planes

The standard definition of torsion angles by Klyne & Prelog (1960) is used.

Plane	CF_3CONH_2 [$X = \text{F}(3)$] dihedral angles	$\text{CClF}_2\text{CONH}_2$ ($X = \text{Cl}$) dihedral angles	$\text{CBrF}_2\text{CONH}_2$ ($X = \text{Br}$) dihedral angles
$X\text{--C}(1)\text{--C}(2)$	180.0°	-75.6°	-77.6°
$\text{F}(1)\text{--C}(1)\text{--C}(2)$	47.0	40.4	150.3
$\text{F}(2)\text{--C}(1)\text{--C}(2)$	-59.7	166.8	38.9
$X'\text{--C}(1)\text{--C}(2)$	139.2	-115.8	-107.0
$\text{F}(1')\text{--C}(1)\text{--C}(2)$	24.1	6.8	(171.6)
$\text{F}(2')\text{--C}(1)\text{--C}(2)$	-109.4	139.5	1.5
$\text{C}(1)\text{--C}(2)\text{--N}$	180.0	2.9	180.0

† The a^* , b , c axis system chosen for ESR measurements corresponds to the monoclinic axis when $P2_1/c$ is chosen rather than $P2_1/n$. Typically, the $P2_1/c$ axes lie parallel or perpendicular to external crystal faces. To convert from the axis system used for ESR measurements to those used for X-ray crystallography simply multiply all ESR directions by the rotation matrix

$$\begin{pmatrix} \cos \alpha & 0 & -\sin \alpha \\ 0 & 1 & 0 \\ \sin \alpha & 0 & \cos \alpha \end{pmatrix}$$

where $\alpha = \beta - 90^\circ$, and β ($= 134.95^\circ$ for CF_3CONH_2) is the $P2_1/c$ monoclinic β angle.

Table 7. Hydrogen-bonded distances and angles

Superscripts denote symmetry codes and refer to molecules related as follows: (i) x, y, z . (ii) $-x, -y, -z$. (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. H peaks were located in the difference map and subsequently refined. The $\text{O}\cdots\text{H}$ distances and $\text{N}\cdots\text{H}\cdots\text{O}$ angles reported are those obtained from the analysis.

		$\text{O}\cdots\text{H}$	$\angle\text{N}\cdots\text{H}\cdots\text{O}$	$\text{N}\cdots\text{O}$
CF_3CONH_2	$\text{N}^{(0)}\text{--H}(1)\cdots\text{O}^{(iv)}$	1.966 (2) Å	164.0 (2)°	2.928 (3) Å
	$\text{N}^{(0)}\text{--H}(2)\cdots\text{O}^{(0)}$	1.976 (2)	161.7 (2)	2.981 (3)
$\text{CClF}_2\text{CONH}_2^*$	$\text{N}^{(0)}\text{--H}(1)\cdots\text{O}^{(iv)}$	1.93 (6)	175 (5)	2.941 (5)
	$\text{N}^{(0)}\text{--H}(2)\cdots\text{O}^{(0)}$	2.37 (6)	153 (6)	3.014 (5)
$\text{CBrF}_2\text{CONH}_2$	$\text{N}^{(0)}\text{--H}(1)\cdots\text{O}^{(iv)}$	2.19 (1)	150 (1)	2.91 (2)
	$\text{N}^{(0)}\text{--H}(2)\cdots\text{O}^{(0)}$	2.31 (1)	122 (1)	3.01 (2)

* Kalyanaram, Kispert & Atwood (1976).

does not equal the separation between the high-field lines ($A - B = 10.25$ G). Rather, this can only be due to two magnetically nonequivalent sites each with slightly different g values resulting from the addition of disorder. As the temperature is raised (Fig. 4b) the spectrum changes to a three-line pattern along with a spectral width increase from 266 to 291 G owing to the torsional oscillation of the CF_2 group (Bogan & Kispert, 1972) about the C—C bond. This effect averages out any observed disorder. The two magnetically nonequivalent sites A and B reappear upon recoiling to 90 K (Fig. 4c) where the motion is frozen out and a different separation of the low-field lines ($A - B = 21.5$ G) and the high-field lines ($A - B = 24.5$ G) is observed owing to an irreversible reorientation of the two magnetically nonequivalent sites.

Further evidence for the presence of disorder is seen in Fig. 5 where an ESR spectrum obtained with the magnetic field parallel to the a^*b plane 35° from the a^* crystal axis is given. The expected two magnetically nonequivalent sites (I) and (II) are observed along with the unequal splittings of the high-field (10.75 G) and low-field (9.75 G) lines. Calculations show that these unequal separations cannot be due to second-order effects. As the temperature is raised (Fig. 5b) the disorder is averaged out.

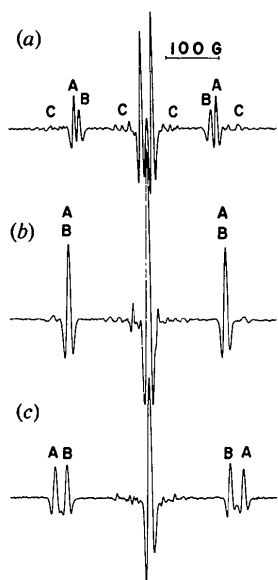


Fig. 4. ESR spectra of irradiated chlorodifluoroacetamide crystals with the magnetic field parallel to the ESR a^* axis when (a) $T = 90$ K and no previous warming, (b) crystal warmed to $T = 170$ K and (c) crystal cooled to $T = 90$ K. The lines A and B indicate the high- and low-field lines of two magnetically nonequivalent sites of $\cdot\text{CF}_2\text{CONH}_2$. Lines C are due to a partially decayed precursor radical.

Examination of the ESR spectrum for irradiated trifluoroacetamide given in Fig. 6 for the magnetic field parallel to the a^* axis shows no evidence for disorder. Detailed examination of the crystal data shows that $\cdot\text{CF}_2\text{CONH}_2$ can only be formed from the primed conformation of (II) and that $\cdot\text{CF}_3$ is rapidly reorienting at 77 K. These effects destroy the possibility of observing disorder in the ESR spectrum at 77 K.

The ESR spectrum of $\cdot\text{CF}_2\text{CONH}_2$ between 77 and 170 K in irradiated bromodifluoroacetamide is obscured by overlapping spectra from precursor radicals, preventing a detailed analysis similar to the

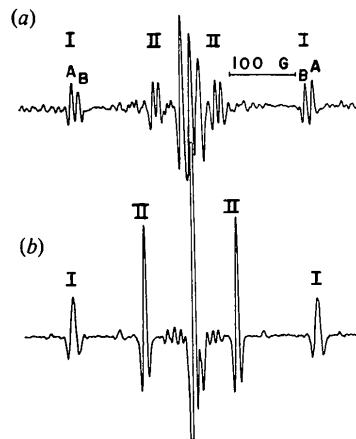


Fig. 5. ESR spectra of irradiated chlorodifluoroacetamide crystals with the magnetic field in the direction $(\cos 35^\circ, 0, \sin 35^\circ)$. (a) The expected monoclinic nonequivalent sites (I) and (II) are split further into lines A and B owing to the appearance of rotational disorder for the $\cdot\text{CF}_2\text{CONH}_2$ radical at 90 K. (b) At 170 K lines A and B for the monoclinic sites (I) and (II) coalesce owing to the known torsional oscillation of the CF_2 group about the C—C bond. The difference in the ESR line width between sites (I) and (II) is because of the appearance of unresolved hyperfine splitting from N and H at certain crystal angles.

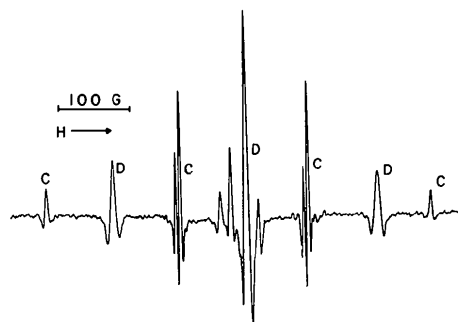


Fig. 6. The ESR spectrum of irradiated trifluoroacetamide at 90 K due to (C) $\cdot\text{CF}_3$ and (D) $\cdot\text{CF}_2\text{CONH}_2$. No unequal splitting of the high- and low-field lines of either radical was observed at any crystal angle between 77 and 200 K, indicating the absence of rotational disorder for the radical observed. The geometry of the unprimed conformation of (II) prevents the loss of F; loss only occurs from the primed conformation.

chloro and fluoro derivatives. Unfortunately, above 170 K, torsional oscillation averages out the presence of any disorder.

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The Crystal Structures of *s*-Triazolo[4,3-*b*]pyridazine, *s*-Triazolo[1,5-*b*]pyridazine and Tetrazolo[1,5-*b*]pyridazine

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The crystal structures of three azolopyridazines have been determined with three-dimensional $Mo K\alpha$ X-ray diffraction data. The crystal data at 20 (1)°C are as follows: *s*-triazolo[4,3-*b*]pyridazine, $C_5H_4N_4$, $M_r = 120.1$, monoclinic, $P2_1/c$, $a = 7.378$ (2), $b = 10.845$ (2), $c = 7.533$ (2) Å, $\beta = 118.78$ (2)°, $V = 528.3$ Å³, $D_m = 1.52$ (5), $D_x = 1.510$ g cm⁻³, $Z = 4$; *s*-triazolo[1,5-*b*]pyridazine, $C_5H_4N_4$, $M_r = 120.1$, monoclinic, $P2_1$, $a = 3.737$ (2), $b = 6.647$ (2), $c = 10.756$ (2) Å, $\beta = 93.30$ (2)°, $V = 266.7$ Å³, $D_m = 1.52$ (5), $D_x = 1.496$ g cm⁻³, $Z = 2$; tetrazolo[1,5-*b*]pyridazine, $C_4H_3N_5$, $M_r = 121.1$, monoclinic, $P2_1/n$, $a = 6.148$ (2), $b = 8.026$ (2), $c = 10.509$ (2) Å, $\beta = 94.84$ (2)°, $V = 516.7$ Å³, $D_m = 1.57$ (5), $D_x = 1.557$ g cm⁻³, $Z = 4$. The structures were solved with direct methods and refined with full-matrix least-squares techniques to R values of 0.055, 0.085, 0.054 and R_w values of 0.053, 0.106 and 0.040 respectively. The molecules are essentially planar. Most of the bond lengths and angles are within normal ranges for aromatic heterocyclic systems, apart from the N(5)–C(6) and C(7)–C(8) bonds in *s*-triazolo[4,3-*b*]pyridazine [1.296 (3) and 1.354 (3) Å] and tetrazolo[1,5-*b*]pyridazine [1.298 (3) and 1.353 (3) Å] which demonstrate a considerable double-bond character.

Introduction

The crystal structures of *s*-triazolo[4,3-*b*]pyridazine (hereinafter STPI), *s*-triazolo[1,5-*b*]pyridazine (STPII) and tetrazolo[1,5-*b*]pyridazine (TP) were determined as

part of a continuing study of the parent bicyclic heterocyclic systems. The present X-ray investigation was motivated by the desire to obtain accurate geometries (bond lengths and angles) of these azolopyridazines with a bridgehead N atom in order to find a possible correlation between the structure and the chemical reactivity.

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