

among the helical chains or the sheets seems generally weak. Some of the shorter contacts among the molecules are shown in Figs. 5 and 6.

The authors are indebted to Professors Shiro Akabori and Shumpei Sakakibara of this Institute for supplying the samples and invaluable advice from the beginning of this project. The authors' thanks are also due to the Matsunaga Science Foundation for its financial support, to the Computation Centre of this University, and to the Computer Centre of the University of Tokyo for making the computers available to them.

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*Acta Cryst.* (1969). **B25**, 1849

## The Structure of *trans-p,p'*-Dichloroazobenzene

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(Received 18 November 1968)

Crystals of *trans-p,p'*-dichloroazobenzene are monoclinic, space group  $P2_1/c$ ,  $a=9.817(5)$ ,  $b=4.708(2)$ ,  $c=11.710(3)$  Å,  $\beta=91.12(5)^\circ$ , with two molecules in the unit cell. Intensity data (Cu  $K\alpha$ ) were obtained with a Picker automatic diffractometer. The structure was refined to  $R=0.049$  for 941 observed reflections. The centrosymmetric molecules are nearly planar. A slight deviation from planarity is discussed. Observed bond distances are: N=N, 1.252; C-N, 1.443; C-Cl, 1.737 Å ( $\sigma \sim 0.005$  Å). Observed angles: N=N-C,  $112.6^\circ$ ; N-C-C (*cis* relative to N=N),  $125.9^\circ$ ; C-C(Cl)-C,  $121.7^\circ$ .

### Introduction

Earlier reports of structure determinations of aromatic azo compounds include the crystal structures of *trans*-azobenzene (Brown, 1966*a*), *trans*-azotoluene (Brown, 1966*b*), *trans*-4,4'-azopyridine *N*-oxide (Eichhorn, 1959), and *trans-p,p'*-dibromoazobenzene (Amit & Hope, 1966). The structures of azobenzene and azotoluene are disordered, making it difficult to obtain accurate results, and the reported standard deviations for distances in the other two compounds are rather large (0.015–0.02 Å).

Since dichloroazobenzene was known to be chemically stable, and since the Cl atoms were expected not to be too heavy to preclude a fairly accurate determination of the parameters for the other atoms, we felt that a structure determination of *trans-p,p'*-dichloroazobenzene might provide more reliable data for the geometry of the azo group.

### Experimental and structure determination

*trans-p,p'*-Dichloroazobenzene was prepared by oxidation of *p*-chloroaniline with sodium perborate in acetic acid (Mehta & Vakilwala, 1952). Crystals were obtained without recrystallization in the form of thin,

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brittle, orange needles. Oscillation and Weissenberg photographs taken with Cu  $K\alpha$  radiation at room temperature showed monoclinic symmetry, with **b** parallel to the needle axis. The systematically absent reflections are  $h0l$  with  $l$  odd and  $0k0$  with  $k$  odd, uniquely indicating the space group  $P2_1/c$ . Preliminary cell dimensions obtained from the photographs suggested the compound to be nearly isomorphous with azotoluene (Brown, 1966*b*) and a survey of the intensity distribution in the  $h0l$  zone gave further indication of this.

Since azotoluene was known to be disordered we decided not to collect a full three-dimensional data set unless *p,p'*-dichloroazobenzene was found not to exhibit disorder. The intensities of the  $h0l$  reflections below  $2\theta = 133^\circ$  were therefore measured rapidly using a Picker automatic diffractometer, and the  $x$  and  $z$  parameters for the Cl atom were determined from a sharpened Patterson function. A Fourier synthesis based on the Cl phases clearly showed the C and N atoms, with no indication of disorder. One cycle of least-squares refinement of the  $x$  and  $z$  parameters and individual isotropic temperature factors gave an  $R$  index of 0.17.

Cell dimensions determined by a least-squares procedure from diffractometer angle measurements are  $a = 9.817(5)$ ,  $b = 4.708(2)$ ,  $c = 11.710(3)$  Å,  $\beta = 91.12(5)^\circ$  [ $\lambda(\text{Cu } K\alpha_1) = 1.54051$  Å,  $t = 23^\circ\text{C}$ ]. The observed density is  $1.55 \text{ g.cm}^{-3}$ , and the calculated density is  $1.54 \text{ g.cm}^{-3}$ , for two molecules per unit cell. (Indexed as azotoluene the cell dimensions would be  $a = 11.710$ ,  $b = 4.708$ ,  $c = 9.817$  Å and  $\beta = 88.88^\circ$ .)

Three-dimensional intensity data were recorded on the automatic diffractometer with Ni-filtered Cu  $K\alpha$  radiation. The crystal, of dimensions  $0.04 \times 0.07 \times 0.2$  mm, was mounted with its long direction (**b**) along the diffractometer  $\phi$  axis. The intensities of 1115 unique reflections with  $2\theta$  less than  $160^\circ$  were measured with the  $2\theta$ - $\theta$  technique at a scan speed of  $0.5^\circ \text{ min}^{-1}$ , with the scan range given by  $[2\theta(\alpha_1) - 1.1^\circ] - [2\theta(\alpha_2) + 1.1^\circ]$ . Background counts were taken for 100 sec at each end of the scan range. Automatic attenuators were used to keep the count rate below 10,000 c.p.s. The intensities of two check reflections (102 and 106) were measured

every 10 hours; all deviations from the means were less than  $\pm 2\%$ .

Corrections were made for Lorentz and polarization effects, but not for absorption or secondary extinction. (With an absorption coefficient of  $51 \text{ cm}^{-1}$  the maxi-

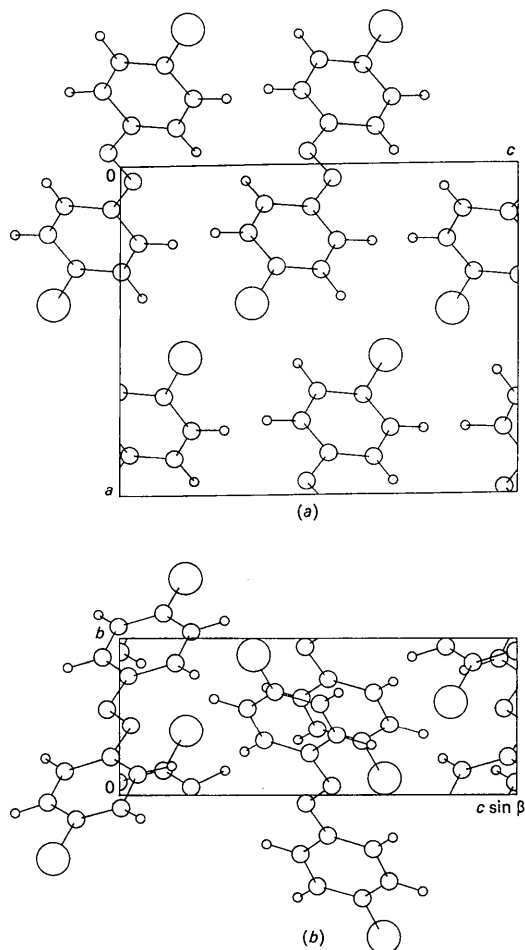


Fig. 1. (a) Projection of the structure along **b**. (b) Projection along **a**.

Table 1. Positional parameters for the atoms of one asymmetric unit, and isotropic thermal parameters for hydrogen atoms

Estimated standard deviations (in parentheses) apply to the least significant digits.

	$x$	$y$	$z$	$B(\text{iso})$
Cl(1)	0.4173 (0.7)	0.9032 (1.6)	0.3342 (0.6)	
C(2)	0.3043 (3)	0.6578 (6)	0.3898 (2)	
C(3)	0.2028 (3)	0.5476 (6)	0.3195 (2)	
C(4)	0.1144 (3)	0.3463 (6)	0.3625 (3)	
C(5)	0.1276 (3)	0.2612 (6)	0.4766 (2)	
C(6)	0.2281 (3)	0.3785 (7)	0.5456 (3)	
C(7)	0.3175 (3)	0.5780 (7)	0.5030 (2)	
N(8)	0.0442 (3)	0.0533 (5)	0.5327 (2)	
H(9)	0.2024 (43)	0.6143 (80)	0.2361 (35)	3.14 (86)
H(10)	0.0437 (40)	0.2687 (94)	0.3127 (33)	2.89 (80)
H(11)	0.2310 (41)	0.3150 (90)	0.6318 (36)	3.28 (86)
H(12)	0.3979 (42)	0.6495 (84)	0.5527 (36)	3.22 (88)

Table 2. Anisotropic thermal parameters

The  $\beta_{22}$ 's have been multiplied by  $10^4$ , all others by  $10^5$ . Estimated standard deviations are given in parentheses.

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl(1)	922 (9)	353 (4)	885 (7)	-637 (24)	507 (11)	150 (22)
C(2)	750 (25)	292 (12)	718 (21)	115 (86)	362 (36)	-68 (75)
C(3)	920 (29)	363 (13)	663 (20)	152 (100)	108 (38)	-194 (86)
C(4)	782 (27)	385 (15)	815 (23)	-336 (98)	62 (39)	-516 (91)
C(5)	795 (26)	318 (14)	802 (22)	147 (96)	412 (38)	-131 (88)
C(6)	967 (30)	417 (16)	685 (21)	-188 (104)	190 (39)	217 (88)
C(7)	912 (29)	408 (15)	694 (21)	-187 (107)	78 (39)	-134 (90)
N(8)	907 (25)	401 (13)	722 (18)	129 (87)	50 (33)	-261 (76)

Table 3. Observed and calculated structure factors ( $\times 10^3$ )

'Unobserved' reflections are marked with U.

h k l	Observed	Calculated	h k l	Observed	Calculated	h k l	Observed	Calculated
0 0 0	1000	1000	10 10 10	100	100	20 20 20	100	100
1 0 0	100	100	11 0 0	100	100	21 0 0	100	100
2 0 0	100	100	12 0 0	100	100	22 0 0	100	100
3 0 0	100	100	13 0 0	100	100	23 0 0	100	100
4 0 0	100	100	14 0 0	100	100	24 0 0	100	100
5 0 0	100	100	15 0 0	100	100	25 0 0	100	100
6 0 0	100	100	16 0 0	100	100	26 0 0	100	100
7 0 0	100	100	17 0 0	100	100	27 0 0	100	100
8 0 0	100	100	18 0 0	100	100	28 0 0	100	100
9 0 0	100	100	19 0 0	100	100	29 0 0	100	100
10 0 0	100	100	20 0 0	100	100	30 0 0	100	100
11 0 0	100	100	21 0 0	100	100	31 0 0	100	100
12 0 0	100	100	22 0 0	100	100	32 0 0	100	100
13 0 0	100	100	23 0 0	100	100	33 0 0	100	100
14 0 0	100	100	24 0 0	100	100	34 0 0	100	100
15 0 0	100	100	25 0 0	100	100	35 0 0	100	100
16 0 0	100	100	26 0 0	100	100	36 0 0	100	100
17 0 0	100	100	27 0 0	100	100	37 0 0	100	100
18 0 0	100	100	28 0 0	100	100	38 0 0	100	100
19 0 0	100	100	29 0 0	100	100	39 0 0	100	100
20 0 0	100	100	30 0 0	100	100	40 0 0	100	100
21 0 0	100	100	31 0 0	100	100	41 0 0	100	100
22 0 0	100	100	32 0 0	100	100	42 0 0	100	100
23 0 0	100	100	33 0 0	100	100	43 0 0	100	100
24 0 0	100	100	34 0 0	100	100	44 0 0	100	100
25 0 0	100	100	35 0 0	100	100	45 0 0	100	100
26 0 0	100	100	36 0 0	100	100	46 0 0	100	100
27 0 0	100	100	37 0 0	100	100	47 0 0	100	100
28 0 0	100	100	38 0 0	100	100	48 0 0	100	100
29 0 0	100	100	39 0 0	100	100	49 0 0	100	100
30 0 0	100	100	40 0 0	100	100	50 0 0	100	100
31 0 0	100	100	41 0 0	100	100	51 0 0	100	100
32 0 0	100	100	42 0 0	100	100	52 0 0	100	100
33 0 0	100	100	43 0 0	100	100	53 0 0	100	100
34 0 0	100	100	44 0 0	100	100	54 0 0	100	100
35 0 0	100	100	45 0 0	100	100	55 0 0	100	100
36 0 0	100	100	46 0 0	100	100	56 0 0	100	100
37 0 0	100	100	47 0 0	100	100	57 0 0	100	100
38 0 0	100	100	48 0 0	100	100	58 0 0	100	100
39 0 0	100	100	49 0 0	100	100	59 0 0	100	100
40 0 0	100	100	50 0 0	100	100	60 0 0	100	100
41 0 0	100	100	51 0 0	100	100	61 0 0	100	100
42 0 0	100	100	52 0 0	100	100	62 0 0	100	100
43 0 0	100	100	53 0 0	100	100	63 0 0	100	100
44 0 0	100	100	54 0 0	100	100	64 0 0	100	100
45 0 0	100	100	55 0 0	100	100	65 0 0	100	100
46 0 0	100	100	56 0 0	100	100	66 0 0	100	100
47 0 0	100	100	57 0 0	100	100	67 0 0	100	100
48 0 0	100	100	58 0 0	100	100	68 0 0	100	100
49 0 0	100	100	59 0 0	100	100	69 0 0	100	100
50 0 0	100	100	60 0 0	100	100	70 0 0	100	100
51 0 0	100	100	61 0 0	100	100	71 0 0	100	100
52 0 0	100	100	62 0 0	100	100	72 0 0	100	100
53 0 0	100	100	63 0 0	100	100	73 0 0	100	100
54 0 0	100	100	64 0 0	100	100	74 0 0	100	100
55 0 0	100	100	65 0 0	100	100	75 0 0	100	100
56 0 0	100	100	66 0 0	100	100	76 0 0	100	100
57 0 0	100	100	67 0 0	100	100	77 0 0	100	100
58 0 0	100	100	68 0 0	100	100	78 0 0	100	100
59 0 0	100	100	69 0 0	100	100	79 0 0	100	100
60 0 0	100	100	70 0 0	100	100	80 0 0	100	100
61 0 0	100	100	71 0 0	100	100	81 0 0	100	100
62 0 0	100	100	72 0 0	100	100	82 0 0	100	100
63 0 0	100	100	73 0 0	100	100	83 0 0	100	100
64 0 0	100	100	74 0 0	100	100	84 0 0	100	100
65 0 0	100	100	75 0 0	100	100	85 0 0	100	100
66 0 0	100	100	76 0 0	100	100	86 0 0	100	100
67 0 0	100	100	77 0 0	100	100	87 0 0	100	100
68 0 0	100	100	78 0 0	100	100	88 0 0	100	100
69 0 0	100	100	79 0 0	100	100	89 0 0	100	100
70 0 0	100	100	80 0 0	100	100	90 0 0	100	100
71 0 0	100	100	81 0 0	100	100	91 0 0	100	100
72 0 0	100	100	82 0 0	100	100	92 0 0	100	100
73 0 0	100	100	83 0 0	100	100	93 0 0	100	100
74 0 0	100	100	84 0 0	100	100	94 0 0	100	100
75 0 0	100	100	85 0 0	100	100	95 0 0	100	100
76 0 0	100	100	86 0 0	100	100	96 0 0	100	100
77 0 0	100	100	87 0 0	100	100	97 0 0	100	100
78 0 0	100	100	88 0 0	100	100	98 0 0	100	100
79 0 0	100	100	89 0 0	100	100	99 0 0	100	100
80 0 0	100	100	90 0 0	100	100	100 0 0	100	100

imum and minimum  $\mu r$  will be about 0.18 and 0.10 respectively for the given crystal mounting.) Reflections for which the net intensity was less than three times its standard deviation (counting statistics) were recorded as 'unobserved' with the recorded value of  $I_{\text{obs}}$  equal to the larger of  $I_{\text{net}}$  and  $0.7\sigma(I_{\text{net}})$ . The number of 'observed' reflections is 941.

The positional parameters already obtained from the  $(x, z)$  projection of *p,p'*-dichloroazobenzene were found to correspond closely to those of the azotoluene position designated 'molecule rotated through  $-5.0^\circ$ ' (Brown, 1966b), after the transformation  $x=z'$ ,  $y=y'$ ,  $z=0.5-x'$ . As initial  $y$  parameters for C and N atoms we therefore used those given for azotoluene, while the  $y$  parameter for Cl was estimated, assuming the Cl atom to be coplanar with the benzene ring and the C-Cl distance to be 1.74 Å.

These parameters, together with the isotropic temperature factors from the two-dimensional least-squares results, gave an initial  $R$  index of 0.24. One least-squares cycle lowered  $R$  to 0.15. Anisotropic temperature factors for the 'heavy' atoms were then introduced, and the hydrogen atoms were placed in 'calculated' positions. The refinement was concluded with a final  $R$  index of 0.049 after three additional least-squares cycles where all parameters (including individual isotropic temperature factors for hydrogen) were adjusted. The largest shift in the final cycle corresponds to 6% of the corresponding estimated standard deviation.

The final positional and thermal parameters are given in Tables 1 and 2 respectively. Observed and calculated structure factors are listed in Table 3.

The Fourier program used was written by H. Hope. Least-squares refinement was run with a program essentially the same as ACA computer program No. 317, written by P. K. Gantzel, R. A. Sparks, and K. N. Trueblood. The program minimizes the weighted sum of the squares of  $\Delta F$  by a full-matrix routine. The weighting scheme used was that of Hughes (1941) with  $4F_o(\text{min})=6.6$ . The atomic form factors were those of

Hanson, Herman, Lea & Skillman (1964). The isotropic temperature factors are of the form  $\exp(-B \sin^2 \theta/\lambda^2)$  and the anisotropic of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ . The  $R$  index is defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  including observed reflections only. Standard deviations were obtained from the inverse of the normal equation matrix.

### Description of the structure

Projections of the structure along **a** and **b** are shown in Fig. 1. Bond distances and angles calculated from the positional parameters in Table 1 are given in Fig. 2. A 'rigid body' analysis of the thermal motion was carried out (Schomaker & Trueblood, 1968). The major libration axis coincides with the long axis of the molecule, the corresponding root mean square amplitude being  $4.5^\circ$ . The r.m.s. difference between 'observed' and 'calculated' amplitude parameters is  $0.004 \text{ \AA}^2$ , indicating that the rigid body approximation is fairly reasonable. Based on the rigid body model, corrected distances and angles were calculated (Cruickshank, 1961). The corrections were small, with none exceeding two estimated standard deviations; the results are therefore not given in full.

The geometry of the azo group is quite similar to that reported earlier. In *trans-p,p'*-dichloroazobenzene we find an N=N distance of  $1.252 \text{ \AA}$  ('corrected'  $1.255 \text{ \AA}$ ), compared to  $1.243 \text{ \AA}$  in *trans*-azobenzene (Brown, 1966a)  $1.244 \text{ \AA}$  in *trans*-azotoluene (Brown, 1966b),  $1.23 \text{ \AA}$  in *trans*-4,4'-azopyridine-*N*-oxide (Eichhorn, 1959) and  $1.276 \text{ \AA}$  in *trans-p,p'*-dibromoazobenzene (Amit & Hope, 1966).

The N=N distance in aromatic azo compounds thus seems to be close to (or perhaps slightly longer than) the distance estimated from the sum of the covalent bond radii ( $1.24 \text{ \AA}$ ; Pauling, 1960) and certainly longer than the N=N distance in the difluorodiazines (Bohn, 1964; Kuczowski & Wilson, 1963). The angles N=N-C(5) and N-C(5)-C(4) ( $112.6$  and  $125.9^\circ$  respec-

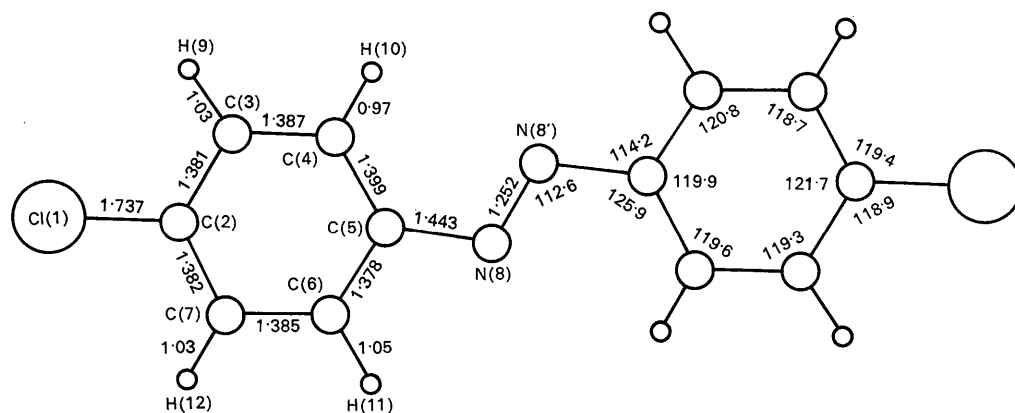


Fig. 2. Bond distances and angles. Estimated standard deviations are  $0.004\text{--}0.005 \text{ \AA}$  for distances not involving H,  $0.04 \text{ \AA}$  for C-H distances and  $0.3\text{--}0.4^\circ$  for angles not involving H.

tively) are very similar to those found in *p,p'*-dibromoazobenzene (112.2° and 125.6° respectively). The C–N distance (1.443 Å) is nearly the same as the corresponding distance in *p,p'*-dibromoazobenzene (1.428 Å). Five of the distances in the benzene ring are very similar, with an average of 1.384 Å (somewhat less than the accepted value of 1.396 Å) whereas the distance C(4)–C(5), (*cis* to the azo group) is 1.399 Å. The apparent lengthening of this bond relative to the others in the ring may not be significant, but we note that in the benzene rings in *p,p'*-dibromoazobenzene the corresponding distance is also somewhat longer than the other five. The C–Cl distance (1.737 Å) is normal (Palenik, Donohue & Trueblood, 1968). The internal angle at C(2), to which Cl is attached, is larger than 120°, in agreement with earlier observations for electron-withdrawing substituents (Carter, McPhail & Sim, 1966; Hope, 1969).

The 'best' plane through the entire molecule (defined by the non-hydrogen atoms) has the equation  $-6.230x + 3.420y + 3.229z = 1.615$  (Å). Individual deviations from this plane are (in Å): Cl(1),  $-0.046$ ; C(2),  $-0.002$ ; C(3),  $0.027$ ; C(4),  $0.028$ ; C(5),  $0.023$ ; C(6),  $0.021$ ; C(7),  $0.009$ ; N(8),  $0.012$ . It is seen that the molecule shows a slight trend towards an 'S' shape, with the Cl atoms being displaced from the ring plane by about 0.05 Å, or more than 50  $\sigma$ . As indicated by the equation of the molecular plane, the perpendicular distance between the rings packed along **b** is near the normal distance of 3.4 Å for aromatic rings. The shortest distance between Cl(1) and a C atom of a neighboring ring (along **b**) is 3.65 Å, in excess of the van der Waals distance. This means that the ring is locked in place, while the Cl atom has some freedom to move in a direction perpendicular to the

molecular plane. An inducement to do so is provided by a Cl–Cl packing contact. The distance between Cl(1) and Cl at  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$  is 3.49 Å, or about 0.1 Å shorter than the sum of the van der Waals radii (3.60 Å); and significantly, the chlorine atom making the contact with Cl(1) is situated on the positive side of the plane given above, while Cl(1) is displaced towards the negative side.

This study has been supported through NSF grant GP-6635.

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## Etude par Diffraction de Neutrons à 0,31°K de la Structure Antiferromagnétique des Grenats d'Aluminium-Terbium et d'Aluminium-Holmium

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(Reçu le 22 novembre 1968)

The crystallographic and magnetic structures of the terbium-aluminum and holmium-aluminum garnets have been determined by neutron diffraction measurements at room temperature, at 4.2°K and 0.31°K. The terbium-aluminum garnet undergoes an antiferromagnetic transition at 1.35°K with an effective magnetic moment of 5.7  $\mu_B$  at 0°K. The holmium-aluminum garnet shows the same antiferromagnetic ordering with a transition temperature of approximately 0.95°K and an effective moment of 5.8  $\mu_B$  at 0°K.

Les grenats d'aluminium-terbium (TbAlG) et d'aluminium-holmium (HoAlG) présentent à très basse température un ordre antiferromagnétique mis en évidence

par des mesures de susceptibilité (Cooke, Thorp & Wells, 1967). Ces mesures donnent des températures de transition de 0,85°K pour HoAlG et de 1,35°K pour