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A Study of the Temperature Variation of Molecular Rotations in Chloranil below T_c

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(*Received* 21 *October* 1980; *accepted* 26 *January* 1981)

Abstract

The variation with temperature of the molecular rotations in chloranil (tetrachloro-*p*-benzoquinone) has been followed below $T_c \simeq 94$ K, within the temperature range 10 to 89 K. The amplitudes of molecular rotations vary continuously with temperature, in agreement with a displacive process. In contrast to early work on the chloranil low-temperature structure, it is shown here that the molecule not only rotates around an axis perpendicular to its plane with a notably larger amplitude than that previously estimated but also performs not negligible rotations around an axis within its plane.

Introduction

At room temperature the chloranil structure is monoclinic, space group $P2_1/a$ (Chu, Jeffrey & Sakurai, 1962). Nuclear quadrupole resonance first revealed the existence of the phase transition at $T_c \simeq 92$ K (Richardson, 1963; Chihara, Nakamura & Tachiki, 1971; Chihara & Nakamura, 1973). As a result of the transition the monoclinic unit cell doubles along the *c* axis and the molecular displacements were considered as corresponding to a staggered rotation about axes perpendicular to the molecular planes (Terauchi, Sakai & Chihara, 1975) (Fig. 1). The low-temperature phase is described as $P2_1/n$ for convenience. A soft mode has been observed in Raman spectroscopy below T_c (Hanson, 1975). Ellenson & Kjems (1977) have used elastic and inelastic neutron scattering to study this transition, particularly the temperature dependence of the order parameter from superlattice Bragg intensities (the critical exponent $\beta = 0{\cdot}33$) and the pronounced softening of the zone-boundary phonon whose eigenvector corresponds to the distortion below T_c. Below 140 K the spectrum also contains a central component diverging at T_c.

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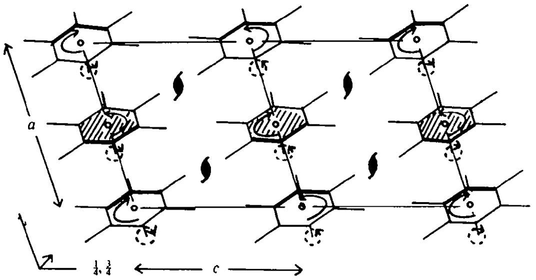

Fig. 1. Molecular rotations in the low-temperature phase of chloranil. Rotations represented in full lines are around the normal *N* to the mean molecular plane (from Terauchi *et al.*, 1975). Rotations represented in dashed lines are around the axis *M* passing through the O atoms (from our analysis of the low-temperature phase). Shaded molecules lie at $\frac{1}{2}b$ above the plane *ac*.

We have reinvestigated in some detail the molecular displacements associated with this phase transition, the proposed low-temperature structure at 77 K in early work having been determined with only eight superlattice reflexions (Terauchi *et al.*, 1975). We have determined the molecular displacements in chloranil over a wide temperature range below T_c, by approaching T_c as near as possible (T_c − 5 K) at a temperature at which a sufficient number of superlattice reflexions are again measurable.

Experimental

The single crystal used, of approximate dimensions 5 × 3·5 × 1·5 mm, was provided by Drs P. Rivet and M. M. Granger in our laboratory. It was grown from a saturated solution in chlorobenzene and was yellow. Unfortunately, the crystal was twinned and attempts to obtain an untwinned crystal of sufficient dimensions (~20 mm^3) for a neutron diffraction study were unsuccessful. However, the risk of confusing a reflexion from the second single crystal with a reflexion of the main single crystal was extremely small: the profile of each reflexion was examined and false reflexions which could occur had a very low probability of being well centred and so could be detected easily. Besides, we have taken care to verify that the superstructure reflexions used in our calculations vanish above T_c. So these reflexions could not be confused with main reflexions of the second single crystal. In fact, a small number of reflexions were rejected.

The experiment was performed on the D15 four-circle neutron diffractometer at the high-flux beam reactor at the Institut Laue–Langevin, Grenoble. A Cu monochromator was used at an incident wavelength λ = 1·179 Å. The cooling unit was a closed-cycle cryogenic refrigeration system employing helium gas as a working medium. A detailed description of the system has already been given (Filhol, Reynal, Savariault, Simms & Thomas, 1980). The cryorefrigerator is a two-stage unit capable of a minimum temperature of 10 K. The long-term temperature stability was within 1 K. Data were collected with the ω scan mode. The intensities of two standard reflexions recorded after every 25 measurements remained constant throughout the data collection.

Molecular rotations in the low-temperature phase

The aim of this study was not to perform a classical and complete refinement of the structure at low temperature. Indeed, chloranil bond lengths and angles are already well known, particularly from the accurate refinement of the high-temperature phase obtained at 110 K by van Weperen & Visser (1972). The chloranil molecule is sufficiently rigid to keep the same geometry at different temperatures: the geometries of the molecule at 110 K and at room temperature (Chu *et al.*, 1962) do not show significant differences. So, the aim was to determine the molecular displacements over a wide temperature range below T_c and mainly as near T_c as possible. Because of the limited time assigned to us on the neutron diffractometer, the number of reflexions measured at each temperature was simply sufficient to permit a refinement by rigid block, the molecular geometry determined by van Weperen & Visser (1972) being imposed in the refinements (Fig. 2).

The measurements were performed at the following four temperatures: 10, 60, 80, 89 K ($T_c \simeq 94$ K). Table 1 gives the cell parameters and the number of reflexions measured at each temperature.

For each molecule the variable geometrical parameters were the three Eulerian angles to allow the molecule to take up any arbitrary orientation in the crystal. Therefore, the total number of geometrical parameters was six for the two independent molecules.

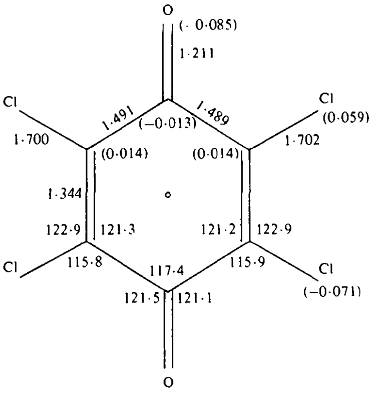

Fig. 2. Geometry of the chloranil molecule (from van Weperen & Visser, 1972) imposed at each temperature in the different constrained refinements. In parentheses are given the deviations from the best plane through the C atoms.

Table 1. *Crystal data and experimental details*

Standard deviations are given in parentheses. $R = \sum (F_{\rm obs} - F_{\rm calc})/\sum F_{\rm obs}$; $R_w = |\sum w(F_{\rm obs} - F_{\rm calc})^2/\sum wF^2_{\rm obs}|^{1/2}$; $w = 1/\sigma_c^2$ where σ_c refers to counting statistics. The number of parameters refined is 13.

T (K)	a (Å)	b (Å)	c (Å)	β (°)	Number of reflexions* (1)	(2)	(3)	(4)	$R(R_w)$	Superlattice reflexions only, $R(R_w)$
10	8·56 (2)	5·59 (1)	16·88 (3)	104·3 (2)	465	263	203	112	0·085 (0·086)	0·086 (0·088)
60	8·62 (2)	5·62 (1)	16·95 (3)	105·7 (2)	327	186	128	71	0·077 (0·081)	0·084 (0·089)
80	8·64 (2)	5·63 (1)	16·98 (3)	105·7 (2)	360	204	152	82	0·085 (0·087)	0·122 (0·125)
89	8·65 (2)	5·64 (1)	17·01 (3)	105·8 (2)	229	131	65	35	0·077 (0·081)	0·112 (0·117)

* (1) Total number of reflexions. (2) Independent reflexions. (3) Total number of superlattice reflexions. (4) Independent superlattice reflexions.

In addition, the same isotropic temperature factor was attributed to atoms which were symmetry-related by the glide plane in the high-temperature phase, giving only six thermal parameters. Anisotropic refinements of the atomic thermal motion were not considered in the low-temperature phase, because of the large number of extra parameters introduced. Under these conditions the ratio between the number of independent observed reflexions and the number of variable parameters varied from 20 (at 10 K) to 10 (at 89 K).

The neutron scattering lengths were $b_{\rm C} = 6{\cdot}63$, $b_{\rm Cl} = 9{\cdot}58$, $b_{\rm O} = 5{\cdot}75$ fm. No corrections were applied for absorption or extinction.

The function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weighting scheme $w^{-1} = \sigma_c^2$ where σ_c^2 refers to counting statistics. In fact, in such a constrained refinement with few variable parameters, the final results are not sensitive to changes in the weighting scheme.

We have found that using 3° (+3° and −3° for the two independent molecules) as the starting value for the tilt angle about the normal to the mean molecular plane and 0° for the other rotations, the positional and thermal parameters quickly converged to stable values, giving conventional R values between 0·077 and 0·085 (Table 1).*

The atomic coordinates and isotropic temperature factors are listed in Table 2 and Fig. 3 gives the tilt angles (averaged for the two independent molecules in the cell) as a function of temperature. It appears first that the molecular displacements below T_c result mainly from a rotation around the normal N to the mean molecular plane, as reported by Terauchi *et al.* (1975), but also from a not negligible rotation about the axis M passing through the two O atoms of the molecule. It should be noted that the tilt angle estimated to be 1·5° at 77 K by Terauchi *et al.* has a larger value at this temperature (about 3·5°) in our analysis. The rotations about the third axis L are negligible.

The tilt angle around the normal N decreases continuously from 5·3° at 10 K, to 2·4° at 89 K. The tilt angle around M decreases from 2·6° at 10 K to 0·6° at 89 K. These variations follow the same law as a superlattice structure factor reported on the same Fig. 3. However, an extrapolation of the two curves above 89 K, our highest experimental point, indicates that φ_M decreases relatively more quickly than φ_N.

This study of the low-temperature phase of chloranil has shown that the transition results from a displacement of the whole molecule considered as rigid. This is a different process from those observed in the recent structural investigations of two molecular crystals exhibiting a displacive phase transition: biphenyl (Cailleau, Baudour & Zeyen, 1979) and *N*,*N*-dimethylnitramine (Filhol, Bravic, Rey-Lafon & Thomas, 1980), where an important change of molecular conformation takes place.

Between 89 K and T_c (94 K), the transition being continuous, superlattice reflexions continue to decrease and vanish at T_c, thermal diffuse scattering becoming important near the transition temperature. The interesting problem as regards physics is what happens to the molecular rotations at $T = T_c$. Do they cancel or not? A response cannot be given from our study since the cancellation of a superlattice reflexion can result from two different processes: (1) the displacive process in which, for each individual molecule, the molecular rotations cancel at T_c, and (2) the order–disorder process in which each molecule oscillating in a double-well potential may reside in two equilibrium positions, the occupancy probabilities of the two sites becoming equal at T_c. Recent theories (Krumhansl & Schrieffer, 1975; Schneider & Stoll, 1976; Aubry, 1976; Bruce & Schneider, 1977) of the mechanism of phase transitions accompanied by a soft mode have postulated a changeover from a displacive regime to an order–disorder regime as T_c is approached from below. Our study of chloranil shows that from 10 to 89 K (T_c = 94 K) the variation of the order parameter, which is

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* Lists of structure factors obtained at 10, 60, 80 and 89 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36009 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times 10^5$), *isotropic temperature factors* (Å^2) *and Eulerian angles* (°) *positioning the molecules in the low-temperature phase*

N, *M*, *L* refer to the molecular axes (Fig. 3). The molecules being considered as rigid blocks in the refinement, the e.s.d.'s are given for the molecular tilt angles (averaged for the two independent molecules).

		First molecule			Second molecule			
		x	y	z	x	y	z	B (σ_B)
$T = 10$ K	C(1)	959	12122	−7392	50294	42531	−8125	0·10 (0·14)
	C(2)	8444	7410	8086	58360	37925	7354	0·74 (0·14)
	C(3)	9706	21432	774	58888	28548	−828	0·25 (0·13)
	Cl(1)	3571	27773	−15602	52082	32092	−17319	0·02 (0·11)
	Cl(2)	19363	17938	17249	69097	22153	15524	0·02 (0·11)
	O	17240	39975	1419	65717	10001	−1561	0·80 (0·16)
			$\varphi_N = 5{\cdot}28$ (0·06)	$\varphi_M = 2{\cdot}64$ (0·09)	$\varphi_L = 0{\cdot}13$ (0·13)			
$T = 60$ K	C(1)	820	11576	−7455	50263	42085	−8041	0·31 (0·18)
	C(2)	8457	7937	8091	58450	38442	7506	0·52 (0·17)
	C(3)	9568	21409	703	58954	28625	−576	0·59 (0·16)
	Cl(1)	3264	26617	−15736	52021	31153	−17111	0·42 (0·14)
	Cl(2)	19374	19057	17254	69295	23259	15879	0·45 (0·14)
	O	16984	39928	1277	65841	10145	−1100	1·08 (0·20)
			$\varphi_N = 4{\cdot}19$ (0·07)	$\varphi_M = 2{\cdot}00$ (0·12)	$\varphi_L = 0{\cdot}08$ (0·18)			
$T = 80$ K	C(1)	805	11124	−7513	50250	41563	−7969	0·61 (0·18)
	C(2)	8408	8360	8027	58500	38948	7580	0·62 (0·17)
	C(3)	9501	21380	568	58996	28610	−416	0·72 (0·16)
	Cl(1)	3223	25655	−15875	51994	30043	−16942	0·71 (0·14)
	Cl(2)	19265	19952	17108	69405	24332	16051	0·62 (0·14)
	O	16859	39874	1025	65922	10117	−801	1·34 (0·21)
			$\varphi_N = 3{\cdot}22$ (0·07)	$\varphi_M = 1{\cdot}28$ (0·12)	$\varphi_L = 0{\cdot}12$ (0·17)			
$T = 89$ K	C(1)	789	10702	−7566	50254	41231	−7913	0·81 (0·22)
	C(2)	8278	8853	7966	58592	39358	7625	0·71 (0·21)
	C(3)	9340	21452	442	59103	28693	−305	0·81 (0·19)
	Cl(1)	3175	24772	−15996	52014	29352	−16813	0·76 (0·17)
	Cl(2)	18971	21008	16966	69610	25214	16157	0·68 (0·16)
	O	16560	39998	788	66124	10265	−592	1·15 (0·25)
			$\varphi_N = 2{\cdot}44$ (0·09)	$\varphi_M = 0{\cdot}56$ (0·15)	$\varphi_L = 0{\cdot}30$ (0·28)			

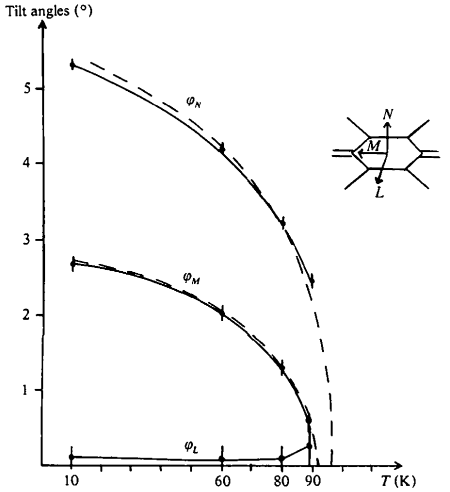

Fig. 3. Tilt angles φ_N, φ_M and φ_L averaged for the two independent molecules, as a function of temperature. In dashed lines are the variations of a superlattice reflexion $\sqrt{I}$, normalized separately for φ_N and φ_M. [I is the intensity for the superlattice reflexion $\bar{1}$,0,3·5 defined in the high-temperature cell (from Ellenson & Kjems, 1977).]

proportional to a superlattice structure factor, results uniquely from molecular rotations, in agreement with a displacive process. However, between 89 K and T_c = 94 K the possibility of an order–disorder regime cannot be discarded.

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Acta Cryst. (1981). B**37**, 1557–1560

Structure de la Phase Ferroélectrique–Ferroélastique du Tanane (Diffraction Neutronique). Evaluation d'Energies de Réseau

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(*Reçu le* 20 *juin* 1980, *accepté le* 26 *janvier* 1981)

Abstract

The structure of the ferroelectric–ferroelastic phase of 2,2,6,6-tetramethylpiperidine 1-oxyl ($C_9H_{18}NO$, 'tanane') was refined from neutron diffraction data [a = 22·64 (2), b = 21·71 (2), c = 8·030 (6) Å, $Fdd2$, Z = 16, 1022 observed reflections, 262 parameters, R_w = 0·06]. The crystal was kept as a single domain by a uniaxial constraint. Little structural change was observed with respect to the tetragonal disordered high-temperature phase. Results of empirical calculations of electrostatic and van der Waals intermolecular energies for the three forms of tanane are in agreement with their domains of stability.

Introduction

Le tétraméthyl-2,2,6,6 pipéridine-oxyl-1 ou 'tanane' est un radical libre de type nitroxyde. Trois phases cristallines ont été répertoriées (Bordeaux, Capiomont, Lajzérowicz, Jouve & Thomas, 1974): une phase haute température quadratique de structure connue (Capiomont & Lajzérowicz, 1974) [groupe d'espace $I\bar{4}2d$, Z = 8, $a = b$ = 15,80 (1), c = 8,130 (6) Å à 293 K], une phase orthorhombique [$Fdd2$, Z = 16, a = 22,64 (2), b = 21,71 (2), c = 8,030 (6) Å à 273 K] et une phase basse température monoclinique de structure également connue (Bordeaux, Lajzérowicz, Brière, Lemaire & Rassat, 1973) [Cm, Z = 2, a = 6,618 (6), b = 14,36 (1), c = 5,879 (5) Å, β = 119,07 (9)° à 291 K].

Le domaine d'existence de la phase quadratique est bien défini et s'étend de la température de fusion t.f. = 311 K à la température T_c = 286,5 K de la transition réversible quadratique–orthorhombique. La phase orthorhombique ne peut être obtenue que par refroidissement de la phase quadratique. La transformation orthorhombique–monoclinique se produit dans des conditions variables et s'accompagne de la réduction en poudre des monocristaux; de plus cette transformation est irréversible puisque la phase monoclinique chauffée se transforme directement en quadratique. La phase orthorhombique doit donc être considérée comme métastable par rapport à la phase monoclinique.

La transition orthorhombique–quadratique qui s'accompagne d'une mise en mouvement de la molécule est du type ordre–désordre, ferroélastique–paraélastique, ferroélectrique–paraélectrique (Bordeaux, Bornarel, Capiomont, Lajzérowicz, Lajzérowicz & Legrand, 1973). De nombreuses études étant en cours sur cette transition et la structure de la phase quadratique désordonnée n'étant qu'approchée, la connaissance de la structure de la phase orthorhombique s'avérait intéressante; nous avons fait sa détermination.

Une fois les structures des trois phases du tanane connues, nous avons entrepris des calculs d'énergie de réseau-énergie de van der Waals et énergie électrostatique (Kitaigorodskii, 1973) – pour essayer, entre

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† Décédée.

* A qui toute correspondance doit être adressée.

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