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MAGNETIC AND OPTICAL PROPERTIES OF AMMONIUM ACID PHTHALATE

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Studies of the principal diamagnetic susceptibilities and refractive indices of ammonium acid phthalate (AAP) crystal of orthorhombic phase are reported. The two properties for the crystal axes a, b and c are of opposite order, i.e., $\chi_a > \chi_b > \chi_c$, while $n_a < n_b < n_c$. Their relations to the structure are offered. The crystal is magnetically unique and optically biaxial with a strong negative optical birefringence. The optical axial plane is parallel to the (010) plane and the molecular one is nearer to the (100) plane. The work gives information on the shape and orientation of the molecules within the unit cell.

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1. Introduction

The present work deals with the study of the magnetic and optical properties of ammonium acid phthalate (AAP), one of a fully known structure [1] among several related salts of phthalic acid [2], with the aim to throw light on their physical anisotropies in relation to their structures. The crystal is orhorhombic with $a = 0.6397$ nm, $b = 1.0231$ nm, $c = 2.6141$ nm, space group $D_{2h}^{15} - P_{cab}, Z = 8$. The compound is essentially ionic, containing ammonium cations and discrete monobasic acid phthalate anions. Each cation is surrounded by six oxygen atoms at distances 0.281 to 0.297 nm apart, in form of a distorted octahedron. The work is devoted to relate these properties to the structure and to give evidence on the molecular shape and orientations.

2. Experimental

Ammonium acid phthalate (AAP, $C_6H_4COOHCOO\ NH_4$) was grown as a crystal with (001) plane face, by slow evaporation of its aqueous solution. Its molecular weight and density are: $M = 183.12$ and $\rho = 1.415$ g/cm^3. The principal diamagnetic susceptibilities, χ_a, χ_b and χ_c were studied by combining the suspension and the Gouy methods, and their molecular values were deduced [3]. The crystal refractive indices n_a, n_b, and n_c were measured using the Becke line method, and the molar refractivities R_a, R_b and R_c were deduced [4].

3. Results and discussion

The measured diamagnetic anisotropies of AAP are listed in Table 1.

The mean diamagnetic susceptibility has been measured by Gouy method [5] to be $\chi_m = -(95.95 \pm 0.17)10^{-6}$ cm^3/mole. The principal susceptibility values χ_i $(i = a, b, c)$ were deduced and are listed in Table 2 together with those of the measured axial refractive indices n_i $(i = a, b, c)$ and their molar refractivities R_i $(i = a, b, c)$.

TABLE 1. Diamagnetic anisotropies of ammonium acid phthalate (AAP) (in units of 10^{-6} cm^3/mole).

Crystal	Diamagnetic anisotropies		
	$\chi_a - \chi_c$	$\chi_a - \chi_b$	$\chi_b - \chi_c$
AAP	50.98 ± 0.06	45.27 ± 0.14	5.71 ± 0.15

TABLE 2. Principal diamagnetic susceptibilities χ_i (in units of 10^{-6} cm^3/mole), refractive indices n_i and molar refractivities R_i (in units of cm^3/mole) of ammonium acid phthalate (AAP).

Property	Principal properties		
	a	b	c
χ_i	128.03 ± 0.83	82.76 ± 0.62	77.05 ± 0.58
n_i	1.501 ± 0.008	1.680 ± 0.006	1.702 ± 0.011
R_i	38.12 ± 0.32	48.89 ± 0.71	50.14 ± 0.53

Figure 1 shows the general relation of χ_i and n_i $(i = b, c)$ to the projection of the AAP molecular plane onto the (100) plane [1]. With increasing knowledge of the exact structure, it should be possible to relate these directional values of χ_i and n_i more precisely to the character of bonds (length, orientation) and hence to the electronic configuration within the structure, but this is out the scope of this work.

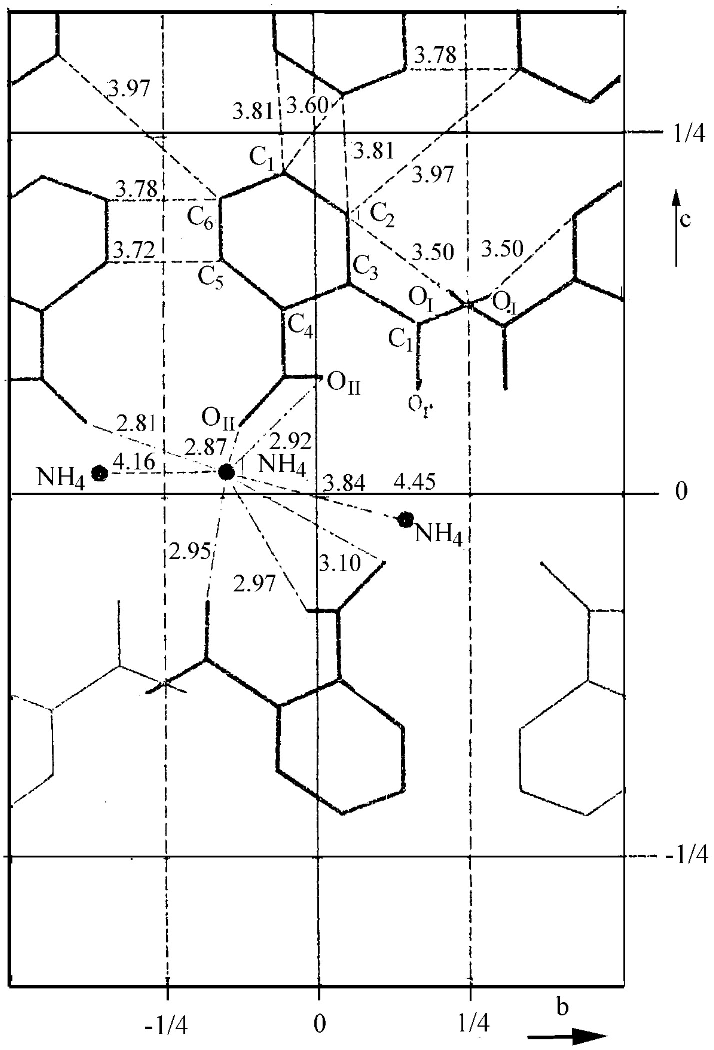

Fig. 1. Projection of the ammonium acid phthalate (AAP) molecular plane onto the (100) plane.

The study exhibits also that ordering of values of diamagnetic susceptibilities is opposite to the ordering of refractive indices, i.e. $\chi_a > \chi_b > \chi_c$, while $n_a < n_b < n_c$. Larger χ_a and smaller n_a, associated with small axial anisotropies of both properties in the bc-plane, suggest that:

1. The molecular plane is inclined to the bc-plane at a small angle, and molecules forming the structure are not parallel but considerably inclined to each other within the molecular plane, in agreement with the X-ray measurements [1]. The anisotropy is due to the anisotropic spreading of the electronic charges within the structure.

2. The structure consists of layers that are parallel to the (100) plane, hence good cleavage parallel to this plane is expected. In the present case, the crystal exhibits perfect cleavage parallel to the (001) plane which is accounted for by the presence of non-polar regions which are formed by contact between benzene rings around the two-fold screw axes at $Z = 1/4$ and 3/4, Fig. 1. [1]. Hence, the crystal is cleaving easily parallel to this plane, and not easy parallel to the spaced layers.

The magnetic measurements exhibit that the crystal is uniquely magnetic along the a axis and exhibits positive magnetic birefringence. The optical data show that the fast vibration direction n_a (minimum index) corresponds to weak binding in this direction. The crystal is biaxial negative with acute optical angle ($2V = 22°56'$) and (010) plane as the optical axial one. Values and orientations of indices suggest large negative optical birefringence of the AAP crystal with molecules of plate like shape [6] that lie in a plane near to the bc-plane. The slow vibration direction n_c (maximum index) is near to the longest axis of the molecule within the molecular plane which contains the polarized oxygen atoms. It was shown earlier [7] that polarization of oxygen atoms is large and their effect on each other is relatively strong. Consequently, the enhanced inductive effect between the oxygen doublets in their distorted octahedron configuration in (AAP) increases the polarization in the molecular plane more than in the normal direction and leads to strong birefringence.

On the other hand, oxygen polarization affects the anisotropy via its magnetic contribution. Electronic paramagnetism is found in miscellaneous compounds with an even number of electrons, including molecular oxygen and organic biradicals [8]. The plane of polarization of incident polarized light is rotated either on reflection (Kerr effect) or on transmission (Faraday effect) by an amount which depends on the magnetization of the compound, which affects the crystal anisotropy [9]. The n_c-direction is characterized not only by high refraction (high polarization) but also high absorption.

To relate the diamagnetic susceptibility to the molecular structure, the molecular magnetic values should be obtained. Knowledge on the molecular orientations with respect to the principal axes a, b, c is required (Table 3.)

TABLE 3. Direction cosines of ammonium acid phthalate (AAP).

	L	M	N
a	0.2081 ± 0.0001	0.4240 ± 0.0022	0.8870 ± 0.0032
b	0.4261 ± 0.0026	-0.8677 ± 0.0061	0.3188 ± 0.0009
c	0.8862 ± 0.0038	-0.1233 ± 0.0007	0.3883 ± 0.0082

The $(L - M)$ plane is a single mean plane which contains the benzene ring and the two carbon atoms of the carboxyl groups. The N-direction is normal to the $(L - M)$ plane.

Using the crystal molecular tensor relation [3], the molecular magnetic values K_L, K_M and K_N as diagonal values, and the molecular magnetic anisotropy ΔK were deduced and are listed together with the molecular values of benzene [3] in Table 4.

TABLE 4. Molecular magnetic susceptibilities, anisotropies of ammonium acid phthalate (AAP) and benzene molecules (in units of 10^{-6}cm^3/mole*).*

Molecule	Molecular magnetic values			Anisotropy
	K_L	K_M	K_N	ΔK
AAP	70.66 ± 0.61	74.08 ± 0.13	142.59 ± 0.63	70.22 ± 0.72
Benzene	34.59 ± 0.82	34.53 ± 0.07	95.35 ± 0.59	60.79 ± 0.06

The angle between the (100) plane and the molecular plane, using the previous relation [3], is $\theta = 27°03'$, in agreement with the result of X-ray measurement [1]. An interesting point arises for the magnetic contribution of the double bond of the carboxyl group within the molecule, which tends to show its presence by a small anisotropy in the L-M molecular plane. The magnetic susceptibility in the normal direction is, however, too large to be attributed only to the presence of these groups of double bonds on the benzene ring, but rather to the benzene ring itself. For aromatic substances with their large conjugated ring systems, it seems that the large molecular orbits of resonance electrons play an important part. Therefore, it appears that the existence of such conjugated bonds implies a force constraining the π electrons to occupy plane orbits of molecular dimensions whose effective area is larger than the normal atomic one, and the weak interaction between the carboxyl group and the benzene ring in the molecule is expected. Similar behaviour is reported in the literature for nitro group substitution on the nucleus, which also increase the molecular magnetic anisotropy [10] associated with weak interaction with benzene ring [11]. In contrast, large interaction between the halogen ion and the benzene ring, as in the previous work [3], leads to a reduction in the molecular orbital motion of π electrons and hence in the molecular magnetic anisotropy. Aromatic ring with substituted conjugated side bonds, as in the present case, results in a larger magnetic anisotropy than that of the aromatic ring alone, because the magnetic contributions are the vectorial sum of those of the constituents [10]. In literature [12], the induced K of $(COOH)_2$ per molecule is about $14 \cdot 10^{-6}$ cm^3/mole, but in the present work it is $10 \cdot 10^{-6}$ cm^3/mole, which may reflect the effect of NH_4 substitution on the conjugation character of its carboxyl group.

4. Conclusion

AAP crystal is magnetically uniaxial along the a axis and optically biaxial with strong negative birefringence. The molecules within the unit cell are inclined to each other in parallel layer planes inclined to the (100) plane at an angle of $27°03'$. The measured properties are oppositely ordered. The work exhibits the effect of double bond in increasing the magnetic and optical anisotropies through its effect on increasing the molecular orbital area of π electrons and polarizability in the molecular plane, respectivelly.

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MAGNETSKA I OPTIČKA SVOJSTVA FTALATA AMONIJEVE KISELINE

Izvješćuju se rezultati istraživanja glavnih dijamagnetskih susceptibilnosti i indeksa loma ortorombske faze kristala ftalata amonijeve kiseline. Dva svojstva za kristalne osi a, b i c su suprotnog redosljeda: $\chi_a > \chi_b > \chi_c$, dok je $n_a < n_b < n_c$. Izlažu se njihovi odnosi sa strukturom kristala. Ovi su kristali magnetski jedinstveni i optički biaksijalni s jakim negativnim dvolomom. Osna optička ravnina je paralelna ravnini (010) a molekulska je bliža ravnini (100). Ovaj rad daje podatke o obliku i orijentaciji molekula unutar jedinične ćelije.