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MAGNETIC ANISOTROPY OF AZOBENZENE CRYSTALS WITH DIFFERENT STEREOSTRUCTURES

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The principal diamagnetic susceptibility of azobenzene $C_{12}H_{10}N_2$ with different stereostructures was measured, and their molecular values were deduced using the molecular-tensor relations. The measurements give evidence on their stereostructures and the shape of conjugation in the crystals. The results give acceptible information concerning the configuration and orientation of the molecules within these molecular crystals. Effect of the contribution of π-electrons on the magnetic anisotropy in crystals is also discussed.

1. *Introduction*

Physical properties of molecular crystals have attracted a wide interest [1-3]. The present work is devoted to the study of diamagnetic anisotropy of some selected crystals of azobenzene of chemical form $C_{12}H_{10}N_2$ with different stereostructures. One of these stereostructures is in the form of monoclinic configuration and the other one is in the form of orthorhombic configuration [4].

The present work gives some information on the effect of stereostructures on the magnetic properties, the planerity and orientation of molecular plane and also on the type of conjugation between the phenyl groups.

2. Experimental

2.1. Investigated crystals

Pure crystals of *trans*- and *cis*azobenzene were grown using a method previously described [5]. The two types of crystals have the same chemical form $C_{12}H_{10}N_2$, but different stereochemical structures. The *trans*azobenzene is of monoclinic structure and *cis*azobenzene is orthorhombic [4]. The diamagnetic susceptibilities of these crystals were determined using the modified method which was previously proposed [6]. Two selected crystals from each type with weights varying between 0.2 and 0.6 mg were used in our measurements.

2.2. Method of calculation

We denote by χ_1, χ_2 and χ_3 the measured axial diamagnetic susceptibilities of the monoclinic *trans*azobenzene crystal and by χ_a, χ_b and χ_c the diamagnetic susceptibilities of the orthorhombic crystal *cis*azobenzene. For monoclinic crystal the molecular diamagnetic susceptibilities K_L, K_M and K_N are obtained from the following relations [7]

$$\chi_i = X_i K_L + Y_i K_M + Z_i K_N \ (i = 1, 2, 3) \tag{1}$$

where

$$\begin{array}{lll} X_1 = \alpha_1^2 + \alpha_1\gamma_1 \tan\varphi & Y_1 = \alpha_2^2 + \alpha_2\gamma_2 \tan\varphi & Z_1 = \alpha_3^2 + \alpha_3\gamma_3 \tan\varphi \\ X_2 = \gamma_1^2 - \alpha_1\gamma_1 \tan\varphi & Y_2 = \gamma_2^2 - \alpha_2\gamma_2 \tan\varphi & Z_2 = \gamma_3^2 - \alpha_3\gamma_3 \tan\varphi \\ X_3 = \beta_1^2 & Y_3 = \beta_2^2 & Z_3 = \beta_3^2 . \end{array}$$

α, β, γ are the known values [4] of the direction cosines of the molecular axes with respect to the crystal axes a, b and c and φ is extinction angle between χ_1 and the a-direction (in the obtuse monoclinic angle β). For orthorhombic crystal the same relation are used but with $\varphi = 0$ and $i = a$, b, c.

3. Results and discussion

For *trans*azobenzene monoclinic crystals, χ_2 is measured parallel to the b-axis, while χ_1 is measured at extinction angle 65.3° with respect to the a-axis in the (010) plane. For *cis*azobenzene orthorhombic crystal the axial values are measured in a, b and c directions. The results are listed in Table 1.

TABLE 1.
Crystal magnetic susceptibilities (10^{-6} cm^3/mole).

Crystal	Axial directions			Extinction angle
*Trans*azobenzene	$\chi_1 = 97.6$	$\chi_2 = 143.5$	$\chi_3 = 96.6$	65.3°
*Cis*azobenzene	$\chi_a = 158$	$\chi_b = 111.2$	$\chi_c = 76.1$	–

These results show that *trans*azobenzene crystals seems to be magnetically uniaxial in the b direction. Small axial anisotropy (χ_1 - χ_3) in the (010) plane and large χ_2 in the normal direction, may suggest, however, that the molecular plane lies in the vicinity of the (010) plane. X-ray diffraction investigation may offer confirmation of these results.

For the *cis*azobenzene only the magnetic ellipsoid is changed and no information could be obtained from these results except that the maximum axial diamagnetic susceptibility appeared in the a direction ([100] direction). That indicates redistribution of the electron density (tighter binding) in this direction.

The calculated molecular diamagnetic susceptibilities K_L, K_M and K_N as diagonal values in the molecular tensor relation are given in Table 2.

TABLE 2.
Molecular magnetic susceptibilities and anisotropies (10^{-6} cm^3/mole).

Molecule	Molecular values			Anisotropy
	K_L	K_M	K_N	ΔK
*Trans*azobenzene	79.2	64.5	192.1	120.25
*Cis*azobenzene	88.7	69.8	190.2	110.95

L is taken parallel to the length of the molecule, M is normal to L in the molecular plane and N is normal to the $(L - M)$ plane as shown in Fig. 1. The molecular anisotropy $\Delta K = K_N - (K_L + K_M)/2$ is also listed in Table 2.

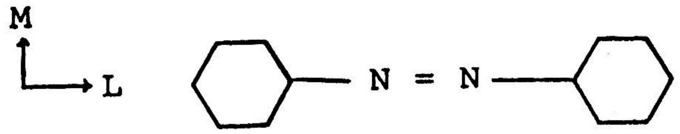

Fig. 1: Structure formula of cis- or transazobenzene $C_{12}H_{10}N_2$.

From these results, it is obvious that the values of K_M and K_L show a marked decrease across the dimensions of the molecule in *trans*azobenzene crystal in comparison with those in *cis*azobenzene crystal, while the normal component K_N is slightly larger in the first crystal. The molecular anisotropy (ΔK) of *trans*azobenzene is larger than that of *cis*azobenzene.

The value of $\Delta K = 120.25{\cdot}10^{-6}$ cm^3/mole obtained for *trans*azobenzene is approximately twice that of the benzene molecule $120{\cdot}10^{-6}$ cm^3/mole [8]. This result indicates that the phenyl group in the molecule, being coplanar, remove any doubt on the inclination of the two phenyl groups. This result is in agreement with the results of X-ray diffraction for this crystal [4]. The value $\Delta K = 110.95{\cdot}10^{-6}$ cm^3/mole for *cis*azobenzene indicates that two phenyl groups in the molecule are not coplanar, but still parallel to each other and twisting of the $N =$ group may be expected. Further X-ray measurement are important to confirm these results. On the other hand the difference in ΔK of the two crystals implies a force constraining π-electrons to occupy plane orbit whose effective area is larger in *trans*azobenzene then that in *cis*azobenzene. Such results were confirmed by others [9] and they throw some light on packing force in these crystals.

4. *Conclusions*

The measurements indicate that *trans*azobenzene seems to be magnetically uniaxial in the (010) direction, and the molecular plane lies in the vicinity of the (010) plane. No information about the inclination of the molecular plane in *cis*azobenzene could be obtained. The value of the molecular anisotropy of *trans*azobenzene ($\Delta K = 120{\cdot}10^{-6}$ cm^3/mole) indicates that its molecule is planar. The slightly smaller anisotropy of *cis*azobenzene ($\Delta K = 110{\cdot}10^{-6}$ cm^3/mole) in comparison with that for *trans*azobenzene indicates that the two phenyl groups in the molecule are not planar. Its two phenyl groups seem to be parallel, but twisting of the $N =$ group may be expected. On the other hand, the difference in ΔK-values indicate that the π-electrons in *trans*azobenzene occupy molecular plane orbit of effective radius more than in *cis*azobenzene.

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MAGNETSKA ANIZOTROPIJA AZOBENZENSKIH KRISTALA RAZLIČITIH STEREOSTRUKTURA

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Mjerena je dijamagnetska susceptibilnost azobenzena $C_{12}H_{10}N_2$ različitih stereostruktura, i njihove molekulske vrijednosti su izvedene primjenom molekulsko-tenzorskih relacija. Mjerenja daju dublji uvid u njihovu stereostrukturu i oblik u kristalima. Rezultati daju prihvatljive podatke o konfiguraciji i orijentaciji molekula u molekulskim kristalima. Raspravlja se također utjecaj doprinosa π-elektrona na magnetsku anizotropiju kristala.