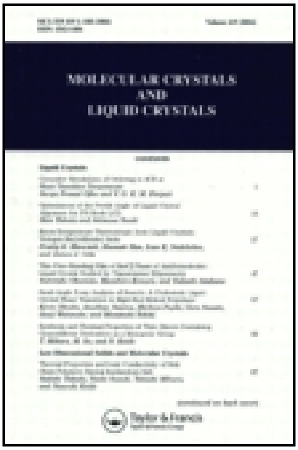

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Orientation and Molecular Structure of 1,5 and 1,8 Dichloroanthraquinones by PMR in a Nematic Solution

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Orientation and Molecular Structure of 1,5 and 1,8 Dichloroanthraquinones by PMR in a Nematic Solution

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The structures and the order parameters of 1,5 and 1,8 dichloroanthraquinones have been determined from the dipolar couplings between the protons in the nematic solutions. The results show the effect of steric interactions on the molecular structure. The aromatic rings of 1,8 dichloroanthraquinone are in different planes making an angle of 15° while 1,5 dichloroanthraquinone appears to be flat. The two molecules show peculiar differences in orientation. The "in-plane" order parameters of the 1,8 derivative are about equal while the 1,5 derivative has a strongly preferred alignment axis close to the Cl, Cl internuclear axis.

I. INTRODUCTION

The orientation of anthraquinone dyes in nematic liquid crystals is of interest for dichroic displays. It has been investigated experimentally and theoretically in recent papers.[1-5] Dichroic ratios of nematic solutions were measured and the correlations between order parameters and molecular structures of the dyes were analyzed. As pointed out in the following, it is difficult to establish clear correlations because additional information is needed.

The dichroic ratio is a measure for the degree of order of the transition axis. Substituents affect the transition and the orientation of the transition axis with respect to the molecular frame. Molecular orbital calculations have been made for a number of derivatives[3] which take into account the effect of the substituents on the transitions. The complete description of the molecular order requires two or three parameters depending on the molecular symmetry. The complete set can be obtained for simple anthraquinone derivatives by PMR. The PMR spectra contain, in addition, information on molecular structures and allow to study distortions of the molecular frame induced by the substituents.

We report in this paper PMR studies on 1,5 and 1,8 dichloroanthraquinones (1,5 ClAQ and 1,8 ClAQ). Both molecules have only six protons (Figure 1). The chlorine substituents are relatively bulky and tend to induce distortions. X-ray studies on solid crystals show that the structure of

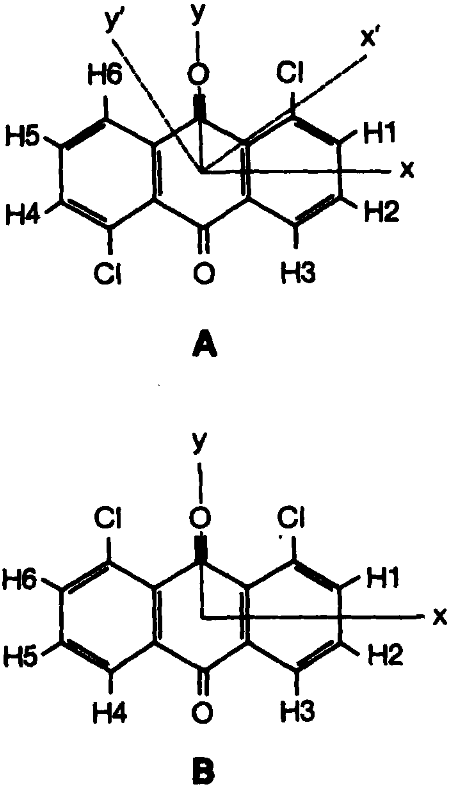

FIGURE 1 Molecular axes system and numbering of protons: (A) 1,5 Dichloroanthraquinone, and (B) 1,8 Dichloroanthraquinone.

1,5 ClAQ is essentially flat[6] but the aromatic rings of 1,8 ClAQ are in planes that make an angle of about 13° with each other.[7] Similar deviations from planarity may occur in nematic solutions and may have some effect on the molecular orientation.

II. EXPERIMENTAL SECTION

Commercially available samples of 1,5 and 1,8 dichloroanthraquinones were used without further purification. Solutions of about 2 wt.% were made in *n*-(p-ethoxybenzylidene)p-n-butylaniline (EBBA) with 1,5 ClAQ and in *n*-(p-methoxybenzylidene)p-n-butylaniline (MBBA) with 1,8 ClAQ. EBBA was used for 1,5 ClAQ because of poor solubility. The spectra were recorded on the Bruker 270 MHz NMR spectrometer in the FT mode at 55° and 19°C respectively with a pulse width of 5μs. The average linewidth was about 5 Hz. The spectra of both compounds were also recorded in an isotropic solution with CCl_4 as the solvent.

III. ANALYSIS OF THE SPECTRA AND RESULTS

The spectra were analyzed on a Burroughs B6800 computer with the aid of an iterative program LAOCOONOR.[8] The isotropic spectra were used for the determination of the scalar spin-spin couplings. The scalar inter ring couplings between the protons are negligible. The scalar intra ring couplings are close to the corresponding couplings of unsubstituted benzene, accordingly, they were assumed to have positive signs. Only chemical shifts and direct dipolar couplings were adapted in the analysis of the anisotropic spectra. The number of transitions assigned were 105 for 1,5 ClAQ and 126 for 1,8 ClAQ. The RMS errors between the observed and the calculated line positions were 1.26 and 0.64 Hz respectively. The theoretical and experimental spectra are shown in Figures 2 and 3. Coupling constants and chemical shifts are given in Tables I and II together with the errors as obtained from the program. Table I shows that the errors of dipolar couplings D_{12}, D_{13} and D_{23} and the chemical shifts are large. In fact, the sums $D_{12} + D_{13} + D_{23}$ and $D_{12} \cdot D_{13} + D_{13} \cdot D_{23} + D_{12} \cdot D_{23}$ can be determined much more precisely than the individual coupling constants. However, within the precision reported, the individual couplings can also be determined.

On the assumption that the molecules have a planar structure 1,5 ClAQ has C_{2h} symmetry and 1,8 ClAQ has C_{2v} symmetry. There are three order

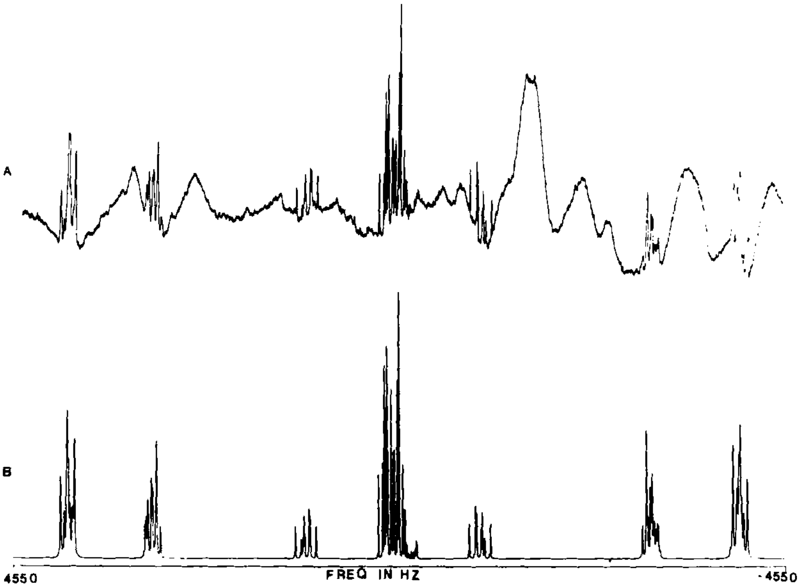

FIGURE 2 (a) Experimental, and (B) theoretical spectrum of 1,5 Dichloroanthraquinone in EBBA at 55°C.

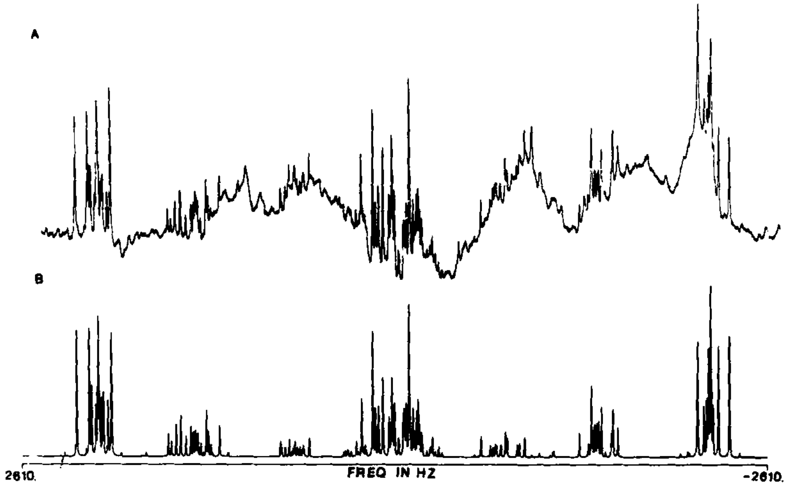

FIGURE 3 (A) Experimental, and (B) theoretical spectrum of 1,8 Dichloroanthraquinone in MBBA at 19°C.

TABLE I

Coupling constants and chemical shifts of 1,5 dichloroanthraquinone (see Figure 1a for labelling.)

i,j	D_{ij}	J_{ij}	$\nu_i-\nu_j$
1,2	−727.0 ± 8.0	8.06 ± 0.82	191.4 ± 3.3
1,3	−367.0 ± 6.4	1.43 ± 0.06	
2,3	−2218.6 ± 1.5	7.75 ± 0.08	−130.8 ± 3.4
1,4	−37.3 ± 0.1		
1,5	−32.2 ± 0.4		
1,6	−51.1 ± 0.4		
2,5	−17.4 ± 0.5		
2,6	−17.1 ± 0.2		
3,6	−6.0 ± 0.4		

TABLE II

Coupling constants and chemical shifts of 1,8 dichloroanthraquinone (see Figure 1b for labelling.)

i,j	D_{ij}	J_{ij}	$\nu_i-\nu_j$
1,2	−876.34 ± 0.21	8.06 ± 0.82	26.42 ± 0.22
1,3	−171.92 ± 0.21	1.43 ± 0.06	
2,3	−882.60 ± 0.21	7.75 ± 0.08	−143.62 ± 0.23
1,4	−29.22 ± 0.06		
1,5	−17.09 ± 0.11		
1,6	−18.99 ± 0.16		
2,4	−40.87 ± 0.12		
2,5	−19.01 ± 0.08		
3,4	−131.66 ± 0.14		

parameters necessary to describe the orientation of 1,5 ClAQ and two for 1,8 ClAQ. Each molecule provides nine independent dipolar couplings. This number exceeds the sum of order parameters and geometric parameters.

The program shape[9] was used to deduct the structure and the order parameters from the dipolar coupling constants. The interproton distances are reported in Tables III and IV. The X-ray distances, also given in the tables, were calculated from the data of the carbon skeleton[6,7] assuming that all CH axes bisect the respective C-C-C angles.

TABLE III

Interproton distances of 1,5 dichloroanthraquinone in Å (see Figure 1a for labelling.)

i,j	r_{ij} (NMR)	r_{ij} (X-ray)[6]
1,2	2.43 ± 0.04	2.44
1,3	4.21 ± 0.04	4.23
2,3	2.48*	2.44
1,4	9.34 ± 0.03	9.47
1,5	9.08 ± 0.03	9.13
1,6	7.04 ± 0.03	7.13
2,5	9.47 ± 0.03	9.44
2,6	7.90 ± 0.03	7.91
3,6	6.90 ± 0.03	6.91

*assumed

TABLE IV

Interproton distances of 1,8 dichloroanthraquinone in Å (see Figure 1b for labelling.)

i,j	r_{ij} (NMR) planar	r_{ij} (NMR) planar	r_{ij} (NMR) non-planar	r_{ij} (X-ray)
1,2	2.08	2.48*	2.46*	2.41
1,3	3.89	4.27	4.26*	4.25
2,3	2.48*	2.48*	2.49 ± 0.08	2.47
1,4	7.74	7.73	7.90 ± 0.09	7.96
1,5	9.48	9.26	9.49 ± 0.09	9.51
1,6	9.25	8.87	9.17 ± 0.09	9.27
2,4	7.14	6.93	7.10 ± 0.08	7.13
2,5	9.26	8.97	9.17 ± 0.04	9.15
3,4	4.84	4.67	4.82 ± 0.11	4.89

*assumed

IV. DISCUSSION AND CONCLUSIONS

The NMR interproton distances obtained for 1,5 ClAQ assuming a planar structure (Table III) are in agreement with the X-ray data within error limits. The diagonalization of the order matrix reveals that its principal axis system is rotated by 33.9° against the symmetry axis of the anthraquinone frame (see Figure 1A, primed system).

As mentioned in the introduction X-ray data show that 1,8 ClAQ deviates from planarity but we analyzed the data first assuming a planar structure. The results are given in column 2 and column 3 of Table IV. For the first analysis only the distance r_{23} was fixed. All other distances were varied to give a best fit. The result is unsatisfactory because the distance r_{12} should be near 2.48 Å while the calculated value in column 2 is 2.087 Å. For the second analysis, column 3, we fixed two distances r_{12} and r_{23}. The reproduction of the D_{ij} is somewhat worse, the RMS error increases from 0.17 to 0.23 Hz, but the obtained structure is much more reasonable. However, the inter ring distances are all too short by about 0.2 to 0.3 Å.

The results in column 4 of Table IV are obtained for a non-planar structure with a perpendicular plane of symmetry through the para axis of the quinone part. There are now three independent order parameters. The "mixed" order parameter S_{yz} can be different from zero for the non-planar structure, but it made no significant contribution. It remained practically zero upon iteration and was set zero for the final analysis. The non-planar structure allows a much better reproduction of the experimental couplings. The RMS error reduced to 0.07 Hz. The interproton distances for this structure are in good agreement with the X-ray data. The distances of proton 3 and 4 from the plane through the four other protons turn out to be 0.4 Å. It corresponds to an angle of 15° between the two aromatic rings which compares favorably with the angle of 13° obtained by X-ray.

The order parameters for the two compounds are summarized in Table V. The values for 1,8 ClAQ belong to the non-planar structure (Table IV, column 4). Both molecules align with their planes parallel to the symmetry axis of the nematic host. The overall orientation of 1,5 ClAQ appears to be higher than that of 1,8 ClAQ. It should be remembered, however, that the solvents were different and the comparison of the absolute values has, therefore, to be made with caution. The order parameters in the x,y planes are more significant. The two principal values for 1,8 ClAQ are nearly equal but for 1,5 ClAQ they differ strongly. The axis with the highest positive order parameter for 1,5 ClAQ is near the axis through the chlorines (see Figure 1). The chlorines are fairly bulky and the particular alignment of 1,5 ClAQ may therefore be favored by the requirement for a dense packing. There are, of course, other factors to consider such as the interactions involving local electrical dipole moments and specific dispersion

TABLE V

Order parameters

Compound	S_{xx}	S_{yy}	S_{zz}	S_{xy}
1,5 ClAQ	0.197	0.093	−0.290	0.128
1,5 ClAQ	0.283*	0.007*	−0.290*	
1,8 ClAQ	0.123	0.108	+0.231	

*Refers to the principal axis system, primed system in Fig. 1A.

forces. We have not attempted to estimate the relative importance of the different factors.

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