Dipole Moment, Molecular Conformation and Crystal Structure of 1,4-Bis(dicyanomethylene)cyclohexane

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With the aim of obtaining some knowledge of the molecular conformation of 1,4-bis(dicyanomethylene)cyclohexane,*1 a dipole moment measurement in dioxane solution, and a three dimensional X-ray analysis of the crystal structure were carried out.

The increase in dielectric constant of the solution with concentration (0.416×10^{-3}—1.677×10^{-3} weight fractions) was measured at three temperatures with the use of a heterodyne-double-beat oscillator(1 MHz) constructed in this laboratory, and a pycnometer was used to determine densities. Values of total polarization were then calculated using both the Halverstadt-Kumlers and Guggenheim-Smiths equations. Dipole moment results obtained through the above procedures are shown in Table 1.

TABLE 1. DIPOLE MOMENT OF 1,4-BIS(DICYANOMETHYLENE)CYCLOHEXANE IN DIOXANE (Debye)

Temperature °C	μ(H-K procedure)	μ(G-S procedure)
40.2	2.14	2.31
50.1	2.20	2.36
59.9	2.42	2.53

As can be seen in the table, the dipole moments thus obtained are fairly large and also show a marked temperature dependence. Since the contribution from atomic polarization,(1) which is supposed to play a significant role in this case, has been neglected in calculating the dipole moment values, we must admit, apart from the possibility of a solvent effect, that these values might not necessarily represent the true dipole moment. Still, considering the symmetrical positions of the two dicyanomethylene substituents on the cyclohexane skeleton, and also the two possible conformations of the skeleton (a chair and a twisted-boat), the results obtained here seems to suggest that the molecule of 1,4-bis(dicyanomethylene)cyclohexane exists predominantly as a flexible twisted-boat form in solution. Molecules in a rigid chair conformation should exhibit a much smaller dipole moment temperature dependence,(1) if they showed any real moment due to distortion of molecular symmetry through solute-solvent interactions. The possibility of complex formation, such as a charge-transfer complex,(1,2) is also excluded in the light of the positive temperature dependence of the dipole moment.

Thus, it seems most probable that the molecule exists as a flexible twisted-boat conformer in solution, the libration of the two highly polar substituents on the central skeletion thereby giving rise to a larger value for the average dipole moment.

On the other hand, a three dimensional X-ray analysis of the crystal structure clearly revealed that the molecule of 1,4-bis(dicyanomethylene)cyclohexane takes a chair conformation in the crystalline state. This fact is an interesting contrast with the case of 1,4-cyclohexanedione, where the molecule is known to behave as a flexible twisted-boat conformer, both in solution,(3-5) and in the crystal.(6,7) A strong interaction between adjacent molecules through highly polar and bulky dicyanomethylene substituents, in the 1,4-bis(dicyanomethylene)cyclohexane crystal, must be responsible for the preference of the chair conformation to that of a flexible one which is more preferable for the 1,4-cyclohexanedione molecule because of the possible contribution of its high entropy term to decreasing the free energy.

Crystallographic data are as follows:

Monoclinic; Space group: $P2_1/n$
$a=10.625+0.005$ Å
$b=7.073+0.005$ Å
$c=7.250+0.005$ Å
$\beta=92.30+0.08°$
$Z=2$

Details will be published later in this Bulletin.

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