Importance of Intramolecular Dipolar Interactions in Determining the Configurations of Polysubstituted Succinonitriles in Solution

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Summary The dipole moment of racemic(±)-2,3-dicyano-2,3-diphenylbutane is lower than that of its *meso*-isomer, unlike the values for the corresponding stilbene dichloride diastereoisomers: this fact, together with evidence adduced from related molecules, shows that intramolecular dipolar interactions can have overriding importance in determining the conformation and relative abundance of rotational isomers of diastereoisomers in solution.

AN excellent example of a molecule existing in two diastereoisomeric forms in which the dipole moments of the *meso*- and racemic (±)-modifications are strikingly different, is stilbene dichloride.[1] Eliel has advanced reasons for expecting the dipole moment of the racemic (±)-form (2·75D) of this molecule to be higher than that of its *meso*-stereoisomer (1·27D). We have found that in at least one system in a series of phenyl-substituted succinonitriles, the *reverse* situation can occur, *i.e.* the racemic (±)- can have a lower moment than its *meso*-isomer. In the original argument,[1] it was pointed out that in the *meso*-compound, the most favoured rotamer is the *trans*-(I) in which the interactions between the bulky phenyl groups and the repulsions between the C–Cl dipoles are simultaneously minimised. The effective moment of the *meso*-form should therefore be relatively low. In the racemic (±)-system however, the preferred conformation should be (V) since the bulky phenyl groups would tend to adopt the antiparallel configuration. Consequently, the overall dipole moment of the racemic form would be comparatively high, *i.e.* higher than that of the *meso*-isomer.

However, if dipolar repulsions between the C–X dipoles were to override steric interactions between phenyl groups in importance, the overall effect could be a higher moment for the *meso*-, compared with the racemic isomer. This situation occurs in 2,3-dicyano-2,3-diphenylbutane (Table 1) which contains two highly polar groups with group moments of *ca.* 3·6D compared with *ca.* 1·6D for the C–Cl bond, and seems best explained in terms of the above effect, the most stable configuration in the racemic (±)-isomer now being (IV) (non-polar) rather than (V) (polar). In the *meso*-isomer, the most stable rotamer in solution would, of course, still be (I). The comparative magnitudes of the diastereoisomeric moments would then be decided by the relative concentrations of the rotamer (I) or (IV) in solution which in turn depend on the relative stabilising influences of the solvent on the polar rotamers. In 3,4-dicyano-3,4-diphenylhexane, however, the polar interactions are offset to some extent by increased steric effects introduced by the presence of two bulky ethyl groups, with the result that the relative

TABLE 1

Dipole moments of some polysubstituted succinonitriles at 25°

Solvent	Solute	Dipole moment (D)	
Dioxan	2,3-Dicyano-2,3-diphenylbutane	*meso*	3·35
		(±) pair	3·09
Benzene	3,4-Dicyano-3,4-diphenylhexane	*meso*	2·64
		(±) pair	3·17
Dioxan	2,3-Dicyano-2,3-dimethylbutane		2·92
Carbon tetrachloride	2,3-Dicyano-2,3-dimethylbutane		2·13
Benzene	2,3-Dicyano-2,3-dimethylbutane		2·78

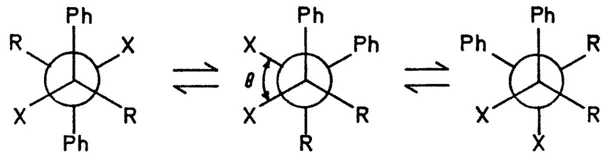
sizes of the moments are reversed again. Even then, the moment of the (±) racemic exceeds that of the *meso*-isomer by the comparatively small figure of 0·53D.

The importance of polar interactions in derivatives of succinonitrile is also manifested in other ways. (i) The dihedral angle θ [Structure (II)] in the gauche rotamer of succinonitrile itself has the unusually large value of 90° which is almost equalled by a corresponding angle of 85° in 2,3-dicyano-2,3-dimethylbutane.[3] Normal dihedral angles[4] fall in the range 60—70°. (ii) Contrary to expectations based on the smaller size of the methyl group compared with phenyl, the gauche population in dioxan of 2,3-dicyano-2,3-dimethylbutane, instead of being significantly higher than that of *meso*-2,3-dicyano-2,3-diphenylbutane (Table 2), is in fact somewhat smaller if the dihedral angles are assumed to be the same, *i.e.* 85°. A corollary to the above statement is the fact that in carbon tetrachloride solution the gauche population of 2,3-dicyano-2,3-dimethylbutane is even less, *i.e.* about 18%, indicating the predominance of the rotamer (I), where the most significant factor is that the highly polar cyano-groups, rather than the methyl groups, are antiparallel. This is a consequence of the fact that in media of different physical characteristics, the polar gauche rotamer is stabilised to different extents by the solvent. Thus there is a striking augmentation of the moment of 2,3-dicyano-2,3-dimethylbutane in the solvents benzene and dioxan relative to carbon tetrachloride[3] (Table 1). In the analogous molecules 2,3-dichloro-2,3-dimethylbutane and 2,3-dibromo-2,3-dimethylbutane which contain much weaker polar groups, the augmentation is markedly less.[5]

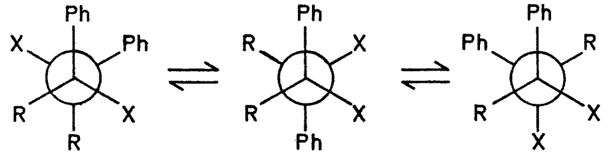
TABLE 2

Population distributions of substituted succinonitriles in dioxan at 25° based on dihedral angle θ = 60—80° [Structure (II)]

Solute	% Gauche rotamer
meso-2,3-Dicyano-2,3-diphenylbutane	33—42
meso-3,4-Dicyano-3,4-diphenylhexane	23—29
2,3-Dicyano-2,3-dimethylbutane	34
(θ = 85° determined experimentally)	31 (in benzene)
	18 (in carbon tetrachloride)



(I) (II) *meso*-form (III)



(IV) (V) (VI)

(±) pair (only one enantiomer shown)

(R = H,Me,Et:X = Cl or CN)

From the above considerations, it may be concluded that polar interactions and solvent effects can be as important as steric factors in the study of the conformations of diastereoisomers.

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