The *meso–dl* Isomerization of 2,3-Dimethyl-2,3-diphenylsuccinonitrile[1]

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Abstract: The *meso* and *dl* diastereomers of 2,3-dimethyl-2,3-diphenylsuccinonitrile have been interconverted both thermally and photochemically. The equilibrium constant (*dl*/*meso*) is 1.22 and is relatively insensitive to temperature. From the rate of isomerization, studied in the 125–175° range, one calculates $\Delta H^{\ddagger} = 42.4$ kcal/mole, $\Delta S^{\ddagger} = 17$ cal/deg mole. The isomerization probably proceeds *via* the 1-phenyl-1-cyanoethyl radical, $C_6H_5(CH_3)\dot{C}CN$, as suggested by trapping experiments with thiophenol and with oxygen. The greater stability of the *dl* isomer, compared to *meso*, implies an attractive interaction between *gauche* cyano groups.

The *meso* and *dl* diastereomers of appropriately substituted ethane derivatives represent classical examples of stereoisomerism. It has been recognized for some time that such configurational isomers are different not only in their physical and chemical properties, but also in their thermodynamic energy contents.[2] However, in spite of the generally accepted energy differences in *meso–dl* systems, very few experimental data are available to support these conclusions. In fact one cannot yet predict with any confidence which isomer is the more stable in even relatively uncomplicated tetra- or hexasubstituted ethanes. Usually it has been assumed that where strong intramolecular attractive forces are present, the *dl* form is thermodynamically more stable than the *meso* and in the absence of such forces that the *meso* isomer is the more stable.[3,4] Although these statements are probably essentially correct, the necessary limitations are not known. Unfortunately much of the experimental evidence which would support these statements is suspect since some of the existing and especially older literature on relative isomer stabilities in these systems is misleading owing to difficulties and attendant errors involved in making structural assignments, determining relative isomer ratios, and establishing equilibrium conditions.

The interconversion of *meso* and *dl* isomers has been observed in only a few isolated instances, and no concerted studies have been made on a related series of such isomers. Of the conventional means for effecting isomerizations, namely, thermal, photochemical, Lewis acid, noble metal, and basic catalysis, only the latter three methods have been employed to interconvert *meso* and *dl* diastereomers in acyclic systems.[5]

Somerville and Spoerri have shown that *dl*-2,3-diphenylbutane is partially converted to the *meso* isomer upon treatment with aluminum chloride.[6a] A similar study by Nenitzescu and Glatz[6b] suggests that the *meso* form may be the more stable. However, in both cases there remains some question as to whether equilibrium conditions prevailed. Buckles, *et al.*,[7] found that the presence of halogens effects the isomerization of *dl*-α,α′-dibromobibenzyl and *dl*-α,α′-dichlorobibenzyl to their *meso* forms. Solid *dl*-α,α′-dibromobibenzyl upon standing in bromine vapor for an extended period reportedly was converted 90% to the *meso* isomer. It should be pointed out, however, that this may not truly reflect the relative free energy differences between the two isomers since crystal lattice forces may be the dominating influence.

dl-2,3-Dimethylsuccinic acid was found to be partially isomerized to the *meso* diacid upon prolonged treatment with acid, leading Linstead and Whalley to conclude erroneously that the *meso* isomer was the more stable.[8] Eberson[9] subsequently has shown that when the *dl*- and *meso*-2,3-dimethyl-, -2,3-diethyl-, and -2,3-diisopropylsuccinic acids are equilibrated with strong hydrochloric acid, the racemic forms predominate. The somewhat unexpected stability of the *dl* isomers was attributed to intramolecular hydrogen bonding between adjacent carboxyl groups. Recently, similar intramolecular interactions have been invoked to explain the predominance of *dl*-2,3-butanediol which arose from the treatment of *meso*-2,3-butanediol with sodium in toluene followed by hydrolysis.[10] *d*-Tartaric acid upon prolonged refluxing with aqueous potassium hydroxide gave a mixture of *dl* and- *meso*-tartaric acid which yielded twice as much *dl* as *meso* upon isolation, however, only about half of the initial tartaric acid was recovered.[2]

Since polyphenylated ethanes are well known to dissociate thermally into polyphenylmethyl radicals, substitution of the phenyls by groups which also will weaken the central carbon–carbon bond either through steric or electronic forces and concurrently satisfy the necessary requirements for *meso* and *dl* isomerism should provide convenient systems for studying the phenomenon of *meso–dl* isomerization. Such compounds

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11–16, 1966.

[2] J. Coope and P. E. Verkade, *Rec. Trav. Chim.*, **44**, 987 (1925).

[3] M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965, p 335.

[4] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 138–139.

[5] Recently, P. D. Bartlett and J. M. McBride (International Symposium on Free Radicals in Solution, Ann Arbor, Mich., Aug 23, 1966) have reported a thermal isomerization wherein *meso*- and *dl*-2,3,4,5-tetramethyl-3,4-diphenylhexane dissociate at 80° into radicals which experience both recombination and disproportionation. At equilibrium, the *meso*/*dl* ratio is approximatly 1.5.

[6] (a) W. T. Somerville and P. E. Spoerri, *J. Am. Chem. Soc.*, **74**, 3803 (1952); (b) C. D. Nenitzescu and A. Glatz, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, **7**, 505 (1959); *Chem. Abstr.*, **54**, 19546*c* (1960).

[7] R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, *J. Am. Chem. Soc.*, **72**, 2496 (1950).

[8] R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 3722 (1954).

[9] L. Eberson, *Acta Chem. Scand.*, **13**, 203 (1959).

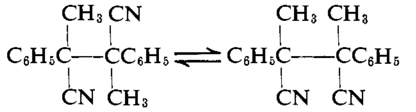
[10] F. Bottari and B. Macchia, *Chim. Ind.* (Milan), **47**, 308 (1965).

are the isomeric *meso*- and *dl*-2,3-dimethyl-2,3-diphenylsuccinonitriles.[11,12] In these compounds, the steric interactions between the various groups are not of the magnitude present in hexaphenylethane, but each substituent is capable of stabilizing the resulting radical through inductive effects or by delocalization of the electron into a π-electronic system.

The present work concerns the study of the *meso–dl* isomerization of the diastereomeric 2,3-dimethyl-2,3-diphenylsuccinonitriles. The results which we now report give some new information with regard to *meso* and *dl* isomer stabilities, and an attempt has been made to clarify some of the factors which influence isomer stabilities in these systems.

Results

When an *o*-dichlorobenzene solution of either the *dl* (I) or *meso* (II) isomer of 2,3-dimethyl-2,3-diphenylsuccinonitrile is heated at 150°, a mixture of the two forms is soon obtained. The isomerization is uncomplicated by potentially undesirable competing reactions such as reaction with solvent molecules, disproportionation,[13] or ketenimine formation.[14] At equilibrium the *dl* isomer predominates with the *dl*/*meso* ratio being about 1.23 (55% *dl* and 45% *meso*). This isomer ratio corresponds to a free energy difference between the two isomers of 0.12 kcal/mole. As can be seen from Table I temperature has a negligible effect on the equilibrium constant.



$$C_6H_5\overset{CH_3}{\underset{CN}{C}}-\overset{CN}{\underset{CH_3}{C}}C_6H_5 \rightleftharpoons C_6H_5\overset{CH_3}{\underset{CN}{C}}-\overset{CH_3}{\underset{CN}{C}}C_6H_5$$

I II

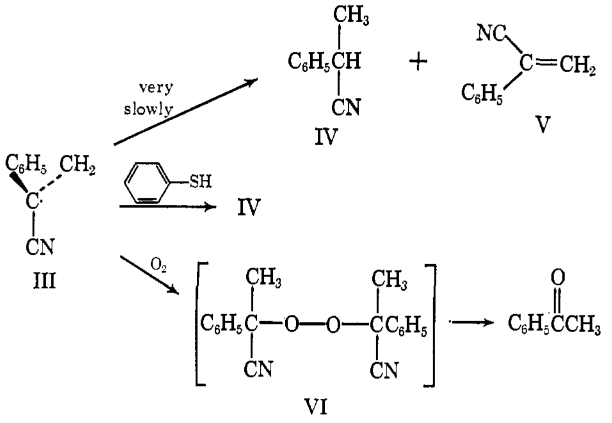
Table I

Temp, °C	% *dl*	k_{eq}	—sec^{-1} × 10^5— $k_{meso\rightarrow dl}$	$k_{dl\rightarrow meso}$	$t_{1/2(meso)}$, hr
125.0	55.3 ± 1.0	1.24 ± 0.05	0.186	0.153	103
150.0	54.9 ± 1.0	1.22 ± 0.05	4.11	3.53	4.7
175.0	55.0 ± 1.0	1.22 ± 0.05	64.5	55.4	0.30

No solvent effect was noted upon the *dl*/*meso* ratio when the isomerization was conducted in tetrachloroethylene, benzonitrile, and nitrobenzene. In all cases the *dl*/*meso* ratio was 1.22 ± 0.05.

The *meso–dl* isomerization of I and II can also be effected photochemically at 25° by irradiating a benzene solution of either isomer at 2537 A. Although the photostationary state has not yet been rigidly established, initial results suggest that the *dl*/*meso* ratio is about 1.0.[15]

The isomerization of I to II appears to proceed by homolytic scission of the central carbon–carbon bond to give methylphenylacetonitrile radicals (III) which then recombine. The ratio of combination to disproportionation must be greater than 100 at 150° since no disproportionation products could be observed over ten half-lives. At 175°, however, after 100 half-lives (>30 hr) a disproportionation product was detected by nmr spectroscopy and gas chromatography, namely, methylphenylacetonitrile (IV). The other product of disproportionation, 1-cyanostyrene (V), was not observed but this is not unexpected since 1,1-disubstituted olefins such as V polymerize readily. When the isomerization was studied in nitrobenzene at 150–160° a much larger amount of disproportionation was observed than in *o*-chlorobenzene (40% *vs.* 0% after 23 hr).



Evidence supporting the radical intermediate III was gained by conducting the isomerization in the presence of a good hydrogen donor. If *meso*-2,3-dimethyl-2,3-diphenylsuccinonitrile is dissolved in thiophenol and the solution heated to 170–180°, quantitative reduction to methylphenylacetonitrile occurs within 2 hr. After only 1 hr in thiophenol, the *dl*/*meso* ratio of the remaining succinonitrile was 0.8 (*vs.* 1.22 at equilibrium), indicating that reduction proceeds at a rate comparable to that of isomerization. The fact that isomerization to the *dl* isomer is observed at all suggests part of the reaction may proceed within a solvent cage or that thiophenol is somewhat inefficient as a radical scavenger.[16]

Oxygen was also found to be a scavenger of methylphenylacetonitrile radicals. When an *o*-dichlorobenzene solution of *meso*-2,3-dimethyl-2,3-diphenylsuccinonitrile was placed under 6 atm of oxygen at 175°, the slow formation of acetophenone was observed. The rate of acetophenone formation appeared to be much slower than the rate of isomerization since less than 10% of the succinonitrile was converted to acetophenone after 24 hr. Again, either a significant portion of the isomerization takes place within a solvent cage[16] or oxygen is a poor scavenger of methylphenylsuccinonitrile radicals. The latter explanation is consistent

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(11) M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, **3**, 97 (1958).

(12) R. L. Huang and L. Kum-Tah, *J. Chem. Soc.*, 2570 (1954).

(13) 2,2,3,3-Tetraphenylbutane dissociates in solution to give 1,1-diphenylethyl radicals which subsequently disproportionate into 1,1-diphenylethane and 1,1-diphenylethylene. See K. Ziegler, *Ann.*, **551**, 127 (1942). Bartlett and McBride observed a similar disproportionation of 2,3,4,5-tetramethyl-3,4-diphenylhexane. At 100° they observed a disproportionation/combination ratio of 0.7.[5]

(14) Recombination of 2-cyanopropyl radicals produced in the thermal decomposition of azobisisobutyronitrile affords dimethylketenecyanoisopropylimine (33%) in addition to tetramethylsuccinonitrile (66%). See M. Taâlt-Erben and S. Bywater, *J. Am. Chem. Soc.*, 77, 3710 (1955).

(15) The isomer ratio obtained at equilibrium should not necessarily correspond to that observed at the photostationary state since the former is thermodynamically controlled whereas the latter should not be. See G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowain, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(16) Experiments are in progress to determine the portion of the isomerization which occurs within the solvent cage. Preliminary results from crossover experiments suggest that the cage effects may be quite small.

with the results of Hartzler who found that the dimerization of dicyanobenzyl radicals was not apparently affected by the presence of oxygen.[17] Although not detected, the peroxide VI seems to be a likely intermediate which would be produced by the reaction of oxygen with III. Thermal decomposition of VI presumably would produce acetophenone.[18]

Attempts to observe the methylphenylacetonitrile radical by electron spin resonance spectroscopy were unrewarding. Even at temperatures up to 300° under conditions where radicals have been observed in similar compounds,[18] no esr signal was detected. A calculation of the equilibrium constant at 300° for dissociation into radicals indicates the radical concentration would be about 10^{-6} *M*, a value approaching the lower limits for detection.

The isomerization of the 2,3-dimethyl-2,3-diphenylsuccinonitriles is conveniently followed by nmr spectroscopy. The methyl protons of the two isomers exhibit distinct resonance peaks which are separated by 0.28 ppm. The methyl absorption of the *meso* isomer occurs at δ 1.80 while that for the *dl* form is found slightly downfield, at δ 2.08.

The rates of the *meso–dl* interconversion were studied at 125.0, 150.0, and 175.0 ± 0.1° in *o*-dichlorobenzene to obtain the activation parameters for the reaction. The *dl*/*meso* ratios were determined periodically until equilibrium was found to be established. The equilibria were approach from both sides in each case. Using the data tabulated in Table II and treating the isomerization as a first-order reversible reaction, rate constants were obtained at each temperature for the conversion of one isomer into the other (see Table I). A plot of the logarithms of the rate constants against the reciprocal of the absolute temperature gave good straight lines (Figure 1). Since the equilibrium constant does not vary significantly with changes in temperature, the activation parameters must therefore be nearly the same for carbon–carbon bond scission in both isomers. The enthalpy of activation, $\Delta H^{\neq}$, was calculated to be 42.4 ± 1.0 kcal/mole and the entropy of activation was found to be about 17 eu.

Inasmuch as the original structural assignments reported for the isomeric 2,3-dimethyl-2,3-diphenylsuccinonitriles were based solely on the melting points of the two isomers, that of the *meso* being higher than that of the *dl*,[12] further characterization was necessary before any conclusions could be drawn regarding relative isomer stabilities. Both isomers were hydrolyzed, therefore, to their respective diacids; the *meso* diacid melted at 224°, while the *dl* diacid melted at 195–196° as anticipated (lit.[19] 196–197°). Thus the structural assignments were confirmed since the *dl* diacid had previously been prepared in an optically active state.

Additionally, both diacids upon heating to their melting points yield anhydrides, the *meso* giving the *cis* anhydride VII (mp 106–107°) and the *dl* affording the *trans* anhydride VIII (mp 159–160°). The nmr spectra of the anhydrides further support the structural assignments since the methyl proton resonance in the *trans* (δ 1.35) was found to be 0.47 ppm upfield from that for the *cis* isomer (δ 1.82, $CDCl_3$). This difference in chemical shift is in accordance with that predicted by the shielding effect of the adjacent phenyl groups.[20]

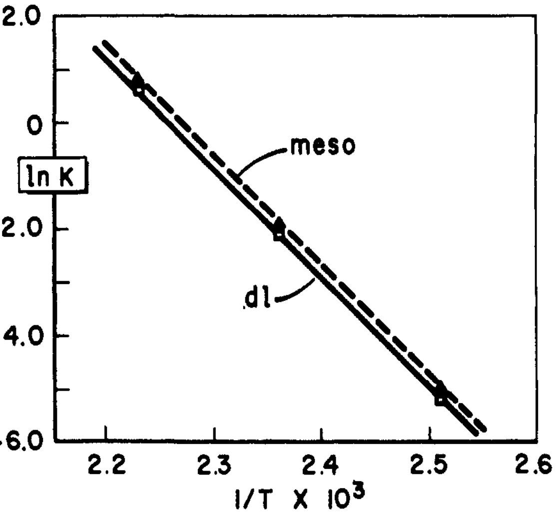
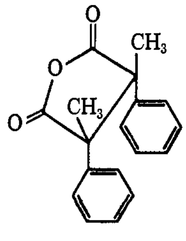
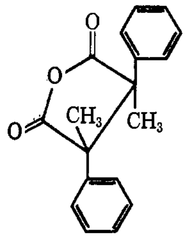


Figure 1. Plot of ln k_{meso} and ln k_{dl} *vs.* the reciprocal of the absolute temperature.



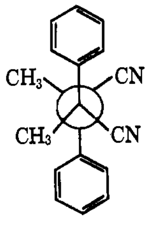
VII



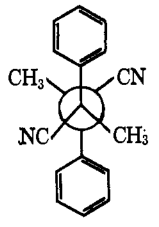
VIII

Discussion

In assessing the relative stability of *meso* and *dl* diastereomers as well as that of the related *erythro* and *threo* isomers, qualitative arguments based primarily on steric factors (nonbonded *repulsive* interactions) have been invoked to explain or predict the free energy differences. In nonpolar compounds where there are no strong attractive interactions (such as the hydrogen bonding present in *vicinal* diols) and therefore where all of the nonbonding interactions between neighboring substituents are essentially of a repulsive nature, the *meso* isomers have been claimed to be more stable than their *dl* counterparts.[3,4] Inspection of Newman projections will show how similar reasoning can be applied to the *meso*- and *dl*-2,3-dimethyl-2,3-diphenylsuccinonitriles.



dl



meso

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(17) H. D. Hartzler, *J. Org. Chem.*, 31, 2654 (1966).

(18) A similar peroxide has been proposed to intervene in the reaction of oxygen with 1,2-dimethoxy-1,1,2,2-tetraphenylethane to afford benzophenone and methyl benzoate. See G. E. Hartzell, C. J. Bredeweg, and B. Loy, *ibid.*, 30, 3119 (1965).

(19) A. McKinzie and A. Ritchie, *Ber.*, **71B**, 643 (1938).

(20) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

In the 2,3-dimethyl-2,3-diphenylsuccinonitriles, *A* values[21] can be used as a measure of the relative steric bulk of each substituent and indicate the order as being phenyl > methyl > cyano.[21,22] If the two isomers are considered in their most preferred conformations, where the phenyl groups are *anti* to one another, then the *gauche* nonbonded interactions can be expressed as follows

$$\textit{gauche}\ \text{interactions}_{dl} =$$

$$2C_6H_5/CH_3 + 2C_6H_5/CN + CH_3/CH_3 + CN/CN \quad (1)$$

$$\textit{gauche}\ \text{interactions}_{meso} =$$

$$2C_6H_5/CH_3 + 2C_6H_5/CN + 2CH_3/CN \quad (2)$$

The difference in nonbonded interactions between the two forms is then

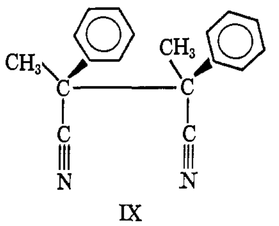
$$\Delta\textit{gauche}\ \text{interactions}_{dl-meso} =$$

$$CH_3/CH_3 + CN/CN - 2CH_3/CN \quad (3)$$

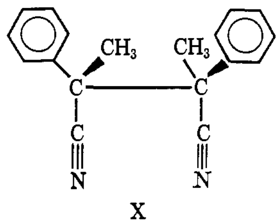
Since the crossed steric interactions between two substituents of unequal size are less than the sum of the interactions between substituents of like size (provided the interactions are purely repulsive in nature), the *meso* isomer would possess less pronounced steric factors and should be adjudged the more stable.[4] A more quantitative treatment of these interactions can be performed by assigning values to the *gauche* interactions which are expressed in eq 3. The *gauche* CH_3/CH_3 (0.85 kcal/mole) and CH_3/CN (0.10 kcal/mole) interactions can be ascertained from the conformational energy difference between the axial and equatorial substituent on a cyclohexane ring.[23] The value of a *gauche* CN/CN interaction is probably less than the comparable CH_3/CN interaction, *i.e.*, less than 0.1 kcal/mole. Insertion of these values in eq 3 indicates that the maximum difference in steric interactions between the *dl* and *meso* forms is then about 0.65 kcal/mole. This undoubtedly is a maximum value since we assumed the two isomers to be in their most preferred conformation. Inasmuch as the other possible conformations are also populated, but probably to a lesser extent,[25] the actual difference in steric interactions is probably less than the calculated value. In considering the other extreme case where there is completely free rotation, and all the conformations are populated to the same extent, one predicts that the steric interactions are the same in both isomers. In view of these extremes, the actual energy difference due to steric repulsions must be between 0.65 and 0 kcal/mole. Additionally, since the values for the *gauche* interactions were obtained from relatively rigid cyclohexane systems, the extension of these quantities to mobile, acyclic systems might introduce considerable error. Consequently, only the direction and not the magnitude of these effects have significance.

Recently it has been pointed out that in considering entropy differences between *meso* and *dl* forms, the *meso* isomer must be compared with the *dl* pair and not simply with one of the active isomers.[26] Since the *d* and *l* isomers are distinctly different species, the entropy change which results from mixing the two forms is $R \ln 2$ and the free energy of the *dl* form is lowered with respect to the *meso* isomer by $RT \ln 2$ due to the entropy of mixing. However, since the *dl* isomer (symmetry number of two) possesses a higher degree of symmetry than the *meso* isomer (symmetry number of unity), reduction of the rotational degrees of freedom in the *dl* form increases its free energy by $RT \ln 2$, thereby offsetting the entropy of mixing. Consequently, the *meso* and *dl* isomers are essentially equivalent entropy-wise, and the relative isomer stabilities are enthalpy controlled.[27]

The foregoing discussion of *gauche* steric interactions (enthalpy differences) in the two isomers predicts the *meso* form should be the more stable and is contradictory to the experimental data. A possible explanation of this discrepancy can be found if one assumes that some of the nonbonded interactions are attractive rather than repulsive. For example, if *gauche* CN/CN interactions give rise predominantly to attractive forces, then substitution of a sufficiently negative value for the *gauche* CN/CN term in eq 3 could more than offset the steric interactions which favor the *meso* isomer.[28] If this were the case, the sum of the nonbonded interactions would be represented by a negative value and the *dl* isomer would be adjudged the more stable form. Qualitatively, this result can also be ascertained from an inspection of the conformation of each isomer where attractive interactions between neighboring cyano groups might be most favorable (IX and X). The steric requirements imposed by the methyl and phenyl groups will obviously be more severe in conformation IX for the *meso* isomer than the comparable conformation for the *dl* form (X) due to the eclipsed or partially eclipsed phenyl groups.



IX



X

Similar explanations involving nonbonded attractive forces, ascribed by some authors to London dispersion forces,[29] have been advanced to rationalize the predominance of the *cis* isomers resulting from the equil-

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[21] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955).

[22] B. Rickborn and F. R. Jensen, *J. Org. Chem.*, 27, 4606 (1962).

[23] One-half of the conformational energy difference between axial and equatorial forms of a methyl and a cyano substituent on a cyclohexane ring provides a good estimate of a *gauche* methyl/methyl and methyl/cyano interaction.[24] Since the conformational free energy difference between an axial and equatorial methyl group is 1.7 kcal/mole and that for cyano is 0.2 kcal/mole, then a *gauche* methyl/methyl interaction is about 0.85 kcal/mole and a *gauche* methyl/cyano is about 0.1 kcal/mole.[22]

[24] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, pp 42–44.

[25] Nmr studies have shown that the *meso-* and *dl*-2,3-diphenylbutanes, -2,3-diacetoxybutanes, and -2,3-dibromobutanes reside in their most preferred conformation less than 70% of the time at room temperature, thus at higher temperatures the most preferred conformations would be occupied to even a lesser extent. See A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, 84, 743 (1962); F. A. L. Anet, *ibid.*, **84**, 747 (1962).

[26] Reference 24, p 25.

[27] The entropy contribution from the differences in symmetry has been pointed out by a referee, and this offsetting term invalidates an earlier explanation[1] of the greater stability of the *dl* isomer.

[28] The literature indicates that *gauche* CH_3/CH_3 and CH_3/CN interactions are both repulsive terms.[21,22]

[29] H. A. Stuart, *Physik. Z.*, **32**, 793 (1931).

ibration of a variety of halogenated olefins including 1-bromo-1-propene,[30] 1,2-dichloroethylene,[31] and 1-fluoro-1,3-butadiene.[32] London forces have also been invoked to explain the anomalous conformational stabilities of some halogenated ethanes.[33]

The existence of attractive nonbonded interactions involving the participation of the nitrile group is not well documented. The predominance of the *cis* isomers upon equilibration of crotononitrile and 3-chloroacrylonitrile, however, may be indicative of this type of interaction.[30] Similarly, the greater stability of the *gauche* over the *trans* conformation in 1,2-dicyanoethane,[34] the preponderance of *cis*-1,2,3-tricyanocyclopropane in the base-catalyzed decarboxylation of *trans*-1,2,3-tricarboethoxy-1,2,3-tricyanocyclo-propane,[35] and the predominance of *cis*-1,2-dicyanocyclobutane in the thermal dimerization of acrylonitrile at 275°[36] could be explained by London dispersion forces between the vicinal cyano groups. Further studies will be necessary to establish the substance of these suppositions.

As was discussed earlier, the free energy differences between *meso* and *dl* isomers is a function of the nonbonded interactions between the various substituents. At this time, it is not yet possible to assess the effect either in direction or magnitude of a given substituent on the relative stability of such diastereomers. Only through a continuing investigation of a related series of *meso* and *dl* isomers will this information be forthcoming. Such a study is in progress.

Experimental Section[37]

The Thermal Isomerization of *meso*- and *dl*-2,3-Dimethyl-2,3-diphenylsuccinonitrile. The *meso* and *dl* isomers of 2,3-dimethyl-2,3-diphenylsuccinonitrile were prepared according to the procedure of Kharasch and Sosnovsky by the Cu(II)-catalyzed oxidative coupling of methylphenylsuccinonitrile.[11] The pure isomers were obtained by fractional crystallization from methanol. The *meso* isomer melted at 224° and the *dl* at 146–147°. The nmr spectra of each isomer revealed no extraneous peaks (*i.e.*, none of the *meso* form was observed in the spectrum of the *dl* isomer, etc.). The *meso* isomer exhibits a methyl resonance peak at δ 1.80 and that for the *dl* isomer came at δ 2.08 ($CDCl_3$).

Solutions of each isomer (0.5 *M*) were prepared in *o*-dichlorobenzene at 80°. The *o*-dichlorobenzene solutions were placed in nmr tubes which were sealed under nitrogen and immersed in a constant temperature bath at the indicated temperatures. The sample tubes were removed periodically and their nmr spectra were run at 80°. The relative areas of the methyl resonance peaks of each isomer were determined by integration. Good reproducibility was obtained in all cases ($\pm 2\%$). The data in Table II were obtained for the thermal isomerizations at 125.0, 150.0, and 175.0 ± 0.1°.

Equilibrium was approached from both directions at each temperature and the same equilibrium constants were obtained within $\pm 0.05\%$. The rate constants shown in Table I were obtained from the foregoing data by simulating the simple first-order reaction sequence on an analog computer and then finding the best fit of the experimental points.

The isomerization was also studied as 0.5 *N* solutions in three other solvents at 150 ± 2° for 3 hr. The following results were obtained (solvent, *dl*/*meso* ratio): tetrachloroethylene, 1.23; benzonitrile, 1.27; and nitrobenzene, 1.22.

Table II

125.0°		15.0°		175.0°	
Time, hr	% *meso*	Time, hr	% *meso*	Time, min	% *meso*
0.0	100.0	0.0	100.0	0.0	100.0
8.0	93.5	1.0	83.7	10.0	73.0
16.0	90.0	2.0	78.0	20.0	60.2
32.0	81.5	3.0	69.9	30.0	52.6
56.0	71.8	4.0	63.9	40.0	48.6
104.0	62.0	5.0	61.5	60.0	46.5
154.0	53.5	7.0	54.0	100.0	45.0
208.0	49.5	9.2	50.0		
300.0	44.7	11.0	48.8		
		15.5	46.0		

Photoisomerization of *meso*-2,3-Dimethyl-2,3-diphenylsuccinonitrile. A benzene solution (100 ml) containing 0.20 g of *meso*-2,3-dimethyl-2,3-diphenylsuccinonitrile was irradiated in a quartz vessel for 17 hr at 40° with 2537-A light from low-pressure mercury lamps (Rayonet photochemical reactor, Southern New England Ultraviolet Co.). The solvent was removed under vacuum at 30°. The nmr spectrum of the resulting solid revealed that isomerization had occurred and the *dl*/*meso* ratio was 0.60. Under the reaction conditions in the absence of light no isomerization takes place. The photoisomerization of the *dl*-2,3-methyl-2,3-diphenylsuccinonitrile to *meso*–*dl* isomer mixture has been effect in a similar manner.

Reduction of *meso*-2,3-Dimethyl-2,3-diphenylsuccinonitrile in Thiophenol. A thiophenol solution 0.5 *M* in *meso*-2,3-dimethyl-2,3-diphenylsuccinonitrile was prepared in an nmr tube. The tube was sealed and placed in a bath at 170–180°. The progress of the reaction was followed by nmr spectroscopy. After 1 hr 90% of the succinonitrile had been converted to methylphenylacetonitrile and the *dl*/*meso* ratio of the remaining 2,3-dimethyl-2,3-diphenylsuccinonitrile was 0.8, indicating that equilibrium had not been reached. After 2 hr, all of the succinonitrile had been reduced to methylphenylacetonitrile. The presence of the acetonitrile was established by peak enhancement of its characteristic nmr spectrum and comparison of the glpc retention time with authentic methylphenylacetonitrile.

Isomerization of *meso*-2,3-Dimethyl-2,3-diphenylsuccinonitrile in the Presence of Oxygen. *o*-Dichlorobenzene (1 ml) containing 25 mg of *meso*-2,3-dimethyl-2,3-diphenylsuccinonitrile was heated at 170° under 100 psi of oxygen for 24 hr. After this period of time, the *dl*/*meso* ratio of the remaining 2,3-dimethyl-2,3-diphenylsuccinonitrile was about 1.2 and a small amount of acetophenone ($\sim 5\%$) was detected by its glpc retention time and its methyl resonance peak in the nmr spectrum of the crude product.

Hydrolysis of the *meso*- and *dl*-2,3-Dimethyl-2,3-diphenylsuccinonitriles. Each dinitrile (0.50 g) was suspended in a solution of 4.0 ml of concentrated sulfuric acid and 4.0 ml of acetic acid in 4.0 ml of water. The resulting suspensions were heated at reflux for 24 hr. The reaction mixtures then were poured into 25 ml of ice water, and the precipitates were collected on filter pads. These solids were dissolved in 20 ml of a 2.5% aqueous solution of potassium hydroxide by heating on a steam bath. The diacids were precipitated upon acidification with dilute hydrochloric acid and recrystallized from benzene. The *meso* dinitrile gave a dicarboxylic acid which melted at 224–225° and the *dl* isomer afforded a diacid melting at 197–198°. The melting point of the *dl* isomer corresponds well with that reported previously (mp 196–197°) for the racemic pair.[19]

Dehydration of the 2,3-Dimethyl-2,3-diphenylsuccinic Acids. Both the *meso*- and *dl*-2,3-dimethyl-2,3-diphenylsuccinic acids lose water upon melting and form an anhydride.[19] The *meso* isomer affords *cis*-2,3-dimethyl-2,3-diphenylsuccinic anhydride, mp 106–107°, and the *dl* isomer yields the related *trans* anhydride, mp 159–160°. The nmr spectrum of the *cis*-anhydride revealed the methyl resonance peak at δ 1.82 and the *trans* form exhibits its methyl peak at δ 1.35 ($CDCl_3$). The infrared spectra of both compounds exhibited strong absorption bands at 1870 and 1798 cm^{-1} characteristic of anhydrides.

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[30] J. W. Crump, *J. Org. Chem.*, **28**, 953 (1963).

[31] K. S. Ditzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1954).

[32] H. G. Viehe, *Angew. Chem.*, **75**, 793 (1963).

[33] Reference 24, pp 15–17, and references therein.

[34] R. J. W. LeFevre, G. L. D. Ritchie, and P. J. Stiles, *Chem. Commun.*, 846 (1966).

[35] G. W. Griffin and L. I. Peterson, *J. Org. Chem.*, **28**, 3219 (1963).

[36] Badische Anilin- and Soda-Fabrik AG., Netherlands Appl. 6,516,357 (June 20, 1966); *Chem. Abstr.*, **65**, 18507 (1966).

[37] Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 instrument. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected.