Tetrahedron Vol 33, pp 273 to 283 Pergamon Press 1977 Printed in Great Britain

DELOCALIZATION ENERGY OF THE CYANOMETHYL RADICAL

KINETICS OF THERMAL DIASTEREOISOMERIZATION OF *CIS*- AND *TRANS*-1,2-DICYANO- AND 1,2-DICYANO-1-METHYLCYCLOPROPANES

W. von E. Doering,* G. Horowitz and K. Sachdev
Department of Chemistry, Harvard University, Cambridge, MA 02138, U.S.A.

(*Received U.S.A.* 26 *April* 1976; *Received U.K. for publication* 16 *August* 1976)

Abstract—Arrhenius parameters for the thermal first-order geometrical isomerization of 1,2-dicyanocyclopropanes(I) have been determined in naphthalene solution over the range 208.0–259.5° in both directions:

$$\log(k_{tc} + k_{ct}) = (14.91 \pm 0.06) - (46.95 \pm 0.13)/\theta;$$

$$\log k_{tc} = (14.24 \pm 0.05) - (46.40 \pm 0.11)/\theta;$$

$$\log k_{ct} = (14.80 \pm 0.06) - (47.20 \pm 0.13)/\theta,$$

where $\theta = 4.575\,T \times 10^{-3}$ and k is in sec^{-1}.
Since this enthalpy of activation is lower than that of the geometrical isomerization of 1,2-dideuterocyclopropane by 17.8 ± 0.4 kcal, it may be concluded that replacement of hydrogen by the cyano group leads to an energy lowering of 8.9 kcal/mol.

Kinetic parameters have been determined in the gas-phase at two temperatures, 217.8° and 259.5°: $\log k_{tc} = 13.73 - 45.64/\theta$; $\log k_{ct} = 13.86 - 44.43/\theta$.

The rates of *cis-trans* interconversion of 1,2-dicyano-1-methyl-cyclopropane(II) relative to those of I have been obtained by examination of mixtures of both substances in t-butylbenzene solution at 259.5°: 1,2-dicyano, $k_{tc} = 1.25$ and $k_{ct} = 3.53$; 1,2-dicyano-1-methyl, $k_{tc} = 8.09$ and $k_{ct} = 22.35 \times 10^{-5}$ sec^{-1}. The rate acceleration by methyl amounts to a factor of 6.4, corresponding to $\Delta\Delta G^{\neq} = 1.96$ kcal/mol. A preliminary examination of optically active material leads to a minimum $R_A = 1.37$ favoring rotation of (CN)(H) over (CN)(CH_3).

In several recent studies of thermal reorganizations,[1-4] the cyano group has been employed advantageously owing to its small steric size, its accelerating effect on rates of rearrangement and its linearity, which represses the intolerable cyclic interaction possible with an ester group[2] and offers noteworthy advantages in the application of the LIS method.[5]

The present work attempts to arrive at a reliable estimate of the stabilizing effect worked on a free carbon radical by an overlapping cyano group. As will appear in the sequel, estimates of this effect have already appeared in the literature and cover a range from 5.5 to 11.6 kcal/mol.

Kinetics offers a general approach to the estimation of the effect of any structural perturbation on the stability of an adjacent radical. The difference in activation energy between that of an unperturbed model and that of the perturbed molecule is taken as the quantitative measure of the effect of the structural perturbation.

In this approach, three major requirements need to be fulfilled. First, the model reaction must in fact involve generation of a radical. Second, the reverse of the process leading to the generation of the radical shall have a known activation energy. (In the absence of an experimental determination of this elusive quantity, the activation energy is customarily assumed to be zero.) Third, the Dewar and Schmeising terms[6] which describe the relative strength of σ bonds in both the transition state and the starting molecule should be negligible.[7]

In the present work, the *cis–trans* isomerization or diastereomerization of cyclopropanes is the basic reaction on which the effect of a perturbation by the cyano group is elucidated. Whether the three requirements are fulfilled is an important question. Instead of a theoretical discussion of each, we prefer to see empirically how well this basic reaction has served in two instances as a vehicle for the determination of radical-stabilizing effects. We hope thereby to instill some confidence in cyclopropane isomerization as a base for the estimation of stabilization by the cyano group.

Stabilization of an adjacent radical by the phenyl group is defined as a combination of an intrinsic benzylic delocalization energy (BDE) and the resultant of four Dewar–Schmeising correction terms.[6] Comparison among these correction terms can be evaluated reliably.

One approach has involved a comparison of the geometrical isomerization of *cis*-stilbene with that of ethylene itself.

From a kinetic study of the reaction of *cis*- to *trans*-stilbene in the gas-phase over the temperature range, 280–342°, Kistiakowsky and Smith[8] obtained a value of 42.8 kcal/mol (log A = 12.77) for the activation energy. Binary m.p. curves were used to determine the composition of the mixtures of *trans*- and *cis*-stilbene. The equilibrium mixture, determined starting from pure *trans*- and pure *cis*-stilbene, contained 6–8% and 17–18% of the *trans*-isomer, respectively. The discrepancy in the two values was attributed to the formation of a liquid by-product when starting with *cis*-stilbene. In the analysis of the kinetic data, an arbitrary correction was made for the liquid by-product and the value of 84% of *trans*-stilbene at equilibrium was taken.

From a kinetic study in the liquid-phase over the temperature range 214–223°, Taylor and Murray reported a value of 36.7 kcal/mol (log A = 10.43).[9] The equilibrium composition was determined in the liquid state at 200° to be 96% *trans* and 4% *cis*-stilbene, starting from either isomer. The reliability of the activation parameters, however, was reduced by the narrow range of temperature over which rate constants were determined.

From a similar study using differential thermal analysis methods, Santor, Banett and Hoyer[10] obtained a value of 46 ± 2 kcal/mol. Although we have used the value of Kistiakowsky and Smith in the sequel, either one of the other values could be used or an average of the three.

The scheme by which BDE may be adduced from a comparison with the geometrical isomerization of ethylene is quite analogous to that put forward by Doering and Beasley for the evaluation of allylic delocalization energy[7] and serves to focus explicit attention on the nature of the Dewar–Schmeising corrections.

$$(1)\quad CH_2{=}CH_2 \rightarrow \overset{\bullet}{C}H_2 \underset{90^\circ}{-} \overset{\bullet}{C}H_2 \qquad \Delta H^{\ddagger} = +63.5\ \text{kcal/mol}$$

$$(2)\quad \varphi CH \underset{cis}{=} CH\varphi + 2H_2 \rightarrow 2\varphi H + CH_2{=}CH_2$$
$$+2E_{C_\varphi C'} + 2E_{HH} + E_* - 2E_{C_\varphi H} - 2E_{HC'}$$

$$(3)\quad \overset{\bullet}{C}H_2 \underset{90^\circ}{-} \overset{\bullet}{C}H_2 + 2\varphi H \rightarrow \varphi \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \varphi + 2H_2$$
$$-2E_{C_\varphi C'^\bullet} - 2E_{HH} + 2E_{C_\varphi H} + 2E_{HC'^\bullet}$$

$$(4)\quad \varphi \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \varphi \rightarrow \varphi \underset{0^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{0^\circ}{-} \varphi \qquad -2\text{BDE}$$

$$\sum_1^4\Big)\quad \varphi{-}CH \underset{cis}{=} CH{-}\varphi \rightarrow \varphi \underset{0^\circ}{-} \overset{\bullet}{C}H \underset{90^\circ}{-} \overset{\bullet}{C}H \underset{0^\circ}{-} \varphi$$
$$\Delta H^{\ddagger} = +41.6\ \text{kcal/mol} = +63.5 - 2\text{BDE} + E_*$$
$$+ 2(E_{C_\varphi C'} - E_{C_\varphi C'^\bullet}) - 2(E_{HC'} - E_{HC'^\bullet})$$

whence

$$\text{BDE} = 11.0 + \tfrac{1}{2}E_* + (E_{C_\varphi C'} - E_{C_\varphi C'^\bullet}) - (E_{HC'} - E_{HC'^\bullet})$$

$$(5)\quad \varphi CH \underset{cis}{=} CH\varphi + H_2 \rightarrow \varphi{-}CH_2CH_2\varphi$$
$$\Delta H_f^\circ(g) = +60.3 \qquad \Delta H_f^\circ(g) = +32.4$$
$$\Delta H_{H_2} = -27.9\ \text{kcal/mol} = E_* - 2E_{C_\varphi C'} - E_{CC} - 4E_{HC}$$
$$+ 2E_{C_\varphi C} - 2E_{HC'}$$

$$(6)\quad CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$$
$$\Delta H_{H_2} = -32.8\ \text{kcal/mol} = -E_{CC} - 6E_{HC} + 4E_{HC'}$$

$$(6){-}(5)\quad \varphi CH_2CH_2\varphi + CH_2{=}CH_2 \rightarrow \varphi CH \underset{cis}{=} CH\varphi + CH_3CH_3$$

whence

$$E_* = (32.8 - 27.9) + 2(E_{C_\varphi C} - E_{C_\varphi C'}) - 2(E_{HC} - E_{HC'})$$

$$\sum_1^4\Big) + (6){-}(5):\quad \text{BDE} = 13.5 +$$
$$(E_{C_\varphi C} - E_{C_\varphi C'^\bullet}) - (E_{HC} - E_{HC'^\bullet})$$

Cyclopropane diastereomerization has also been used as the basis reaction. From the rate constants for the interconversion of *cis*- and *trans*-1,2-diphenylcyclopropane reported by Crawford and Lynch,[11] the kinetic expression can be derived: $\log(k_{t,c} + k_{c,t}) = 10.9 - 34.80/RT \ln 10$ and K = 11.8 at 205°. When the estimated value for $\Delta H^{\ddagger}$, 36.2 kcal/mol, is combined with the value of 63.7 kcal/mol from the geometrical isomerization of 1,2-dideuteriocyclopropane,[12] a value for the benzylic stabilization can be deduced, BDE = 13.8 kcal/mol + $f(C'_\varphi H/CpCp^\bullet)$, where $f(C'_\varphi H/CpCp^\bullet)$ is a convenient contraction of the Dewar–Schmeising correaction terms,

$$(E_{C_\varphi C_p} - E_{C_\varphi C_p^\bullet}) - (E_{HC_p} - E_{HC_p^\bullet}).$$

Similarily, if the enthalpy of activation for the conversion of liquid *cis*-1,2-diphenylcyclopropane found by Rodewald and DePuy[13] ($\Delta H^{\ddagger}$ = 32.6 kcal/mol) is combined with the reported difference of 1.7 kcal/mol in ΔH_f° of *cis*- (+44.3) and *trans*- (+42.7),[14] BDE = 14.7 kcal/mol + $f(C'_\varphi H/CpCp^\bullet)$.

Additional estimates can be derived from the cleavage of other types of covalent bond as the basis reactions.[15] Thus, the observed enthalpy of activation for the dissociation of bibenzyl is reported to be 47.1 kcal/mol, although it must be noted that the low preexponential factor (log A = 9.3) has caused serious doubt to be cast on its validity.[16] This datum combined with the enthalpy of activation of dissociation of ethane ($\Delta H^{\ddagger}$ = 85.1 kcal/mol) leads to BDE = 19.0 + $f(C'_\varphi H/CC^\bullet)$.

Several determinations of the heat of dissociation of the benzyl-hydrogen bond in toluene fall close to 85.0 ± 1 kcal/mol.[17] Comparison of this value with a representative value for the primary C–H bond in ethane or propane, 97.5 kcal/mol, leads to a value for benzyl resonance, BDE = 12.5 + $f(C'_\varphi C/CC^\bullet)$. If methane is used as reference (104.1 ± 0.5 kcal/mol), BDE = 19.1 + $f(C'_\varphi H/CC^\bullet)$.

Bond fission of ethylbenzene at 950°K to benzyl and methyl radical reveals an enthalpy of activation of 68.4 kcal/mol (log A = 14.6),[18] whence BDE = 16.7 + $f(C'_\varphi H/CC^\bullet)$.

Similarly, from the bond dissociation energy of benzyl bromide (50.5 kcal/mol)[19] and $\Delta H_f^\circ(g)$ = 17.0 ± 3.0 kcal/mol,[20] $\Delta H_f^\circ(g)$ of the benzyl radical is 41.0 kcal/mol. Coupled with $\Delta H_f^\circ(g)$ of bibenzyl (+32.4 kcal/mol),[21] a value of BDE = 17.8 + $f(C'_\varphi H/CC^\bullet)$ can be derived.

Finally, from the enthalpies of activation for dissociation of benzyl mercaptan and methyl mercaptan of 51.8 and 65.4 kcal/mol, respectively,[16] a value of BDE = 13.6 + $f(C'_\varphi H/CC^\bullet)$ is obtained.

A reliable value of BDE can hardly be extracted from these various comparisons, 13.5 + $f(C'_\varphi H/CC'^\bullet)$; 14.3 ± 0.5 + $f(C'_\varphi H/CpCp^\bullet)$; 17.2 ± 2.3 + $f(C'_\varphi H/CC^\bullet)$; 12.5 + $f(C'_\varphi C/CC^\bullet)$.

Not only are valid estimations of the Dewar–Schmeising corrections desirable, but even if the assumption is made that the three different types of radical ($C'^\bullet$ in the 90° twisted ethylene, $Cp^\bullet$ in the hypothetical trimethylene diradical and $C^\bullet$ in the common free radical) have comparable correction terms and that activation energies for the reverse reactions are zero, the spread in values is uncomfortably large.

The second illustration from the literature concerns the allylic delocalization energy (ADE) or the perturbation by the vinyl group. The investigation of the *cis–trans* isomerization of trienes leads to a value of ADE = 17.1 + f((C′H/CC′●)[7] which may be compared with values derived from examination of the *cis–trans* isomerizations of cyclopropanes. From the difference between the enthalpy of activation of the *cis–trans* isomerization of 1,2 - dideuteriocyclopropane (63.7 kcal/mol),[22] and two values for the *trans–cis* isomerization of *trans* - 1,2 - divinylcyclopropane ($\Delta H^{\ddagger}$ = 31.2 kcal/mol[22] and 33.1 kcal/mol[23]), a value is found for ADE = 15.8 ± 0.5 + f(C′H/CpCp●). From the isomerization of *trans* - 1,2 - divinyl - 3,3 - dimethylcyclopropane[24] ($\Delta H^{\ddagger}$ = 31.5 kcal/mol), the value, ADE = 16.1 + f(C′H/CpCp●), is obtained. A related comparison depends on the isomerization of *cis* - 1 - deuterio - 2 - vinyl cyclopropane investigated by Willcott and Cargle[25] ($\Delta H^{\ddagger}$ = 47.1 kcal/mol), whence ADE = 16.6 + f(C′H/CpCp●). The average value from the cyclopropanes, ADE = 16.1 ± 0.6 + f(C′H/CpCp●), lies close to the value from the trienes, ADE = 17.1 + f(C′H/CC′●).

Comparisons may also be made on the basis of the replacement of a methyl group by a vinyl group. The Dewar–Schmeising terms then become functions of olefinic (C′) and tetrahedral (C) carbon. From *trans*-butene and hexatriene the value, ADE = 13.1 + f(C′C/CC′●),[7] is obtained while the comparison of *trans* - 1 - methyl - 2 - vinylcyclopropane[26,27] with *trans* - 1,2 - dimethylcyclopropane[28] leads to the values, ADE = 13.3[26] or 10.5[27] + f(C′C/CpCp●). Values of ADE = 12.6[29a] or 10.2[29b] + f(C′C/CC●) based on iodine abstraction of hydrogen atoms in butene-1 and propylene, respectively, and a single value of ADE = 13.4 + f(C′C/CC●) based on pyrolysis of allyl methyl sulfone[30] have been obtained. Here, again, the three different correction factors do not seem to differ significantly among themselves [ADE = 13.1 + f(C′C/CC′●); 11.9 ± 1.4 + f(C′C/CpCp●); 12.1 ± 1.7 + f(C′C/CC●)] but do differ significantly from the first pair [ADE = 17.1 + f(C′H/CC′●); 16.1 + f(C′H/CpCp●)].

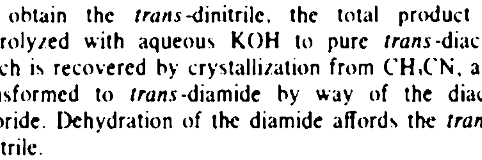
From the examination of both vinyl and phenyl perturbations comes the strong indication that the difference between correction terms of the f(aC/bd) type and the f(aH/bd) type are significant and range from 2 to −4 kcal/mol. As a practical consequence, estimates of empirical lowering of activation energy depend on whether a hydrogen atom or an alkyl group in the standard model is being replaced by the perturbing group.

From this detailed analysis of the phenyl and vinyl perturbations and given the inherent uncertainties in differences between any pair of experimental activation energies, there is little justification for choosing one basis reaction over another, at least not until reliable evaluation of the Dewar–Schmeising correction terms or experimental determination of activation energies of the reverse reactions indicates to the contrary. Cyclopropane isomerization seems as reliable as any of the other reactions as a vehicle for the estimation of perturbations.

The substances used in the present work to evaluate the stabilizing effect of the cyano group are *cis*- and *trans* - 1,2 - dicyanocyclopropanes (I) and their 1-methyl analogs (II). Synthesis of the first pair of dinitriles is effected by dehydration of the diamides, which are prepared from the corresponding dimethyl esters. Dimethyl *cis*- and *trans* - cyclopropane - 1,2 - dicarboxylate, synthesized according to the method of McCoy[11] by the procedure described previously,[1] are converted to the diamides in 80–85% yield by treatment with 30% aqueous NH_4OH. The diamides in turn are conveniently dehydrated by $SOCl_2$ in DMF[12] with benzene as a co-solvent, to the dinitriles in 60–65% yield. Chromatographically pure samples of both the *cis*- and the *trans* - dinitriles are characterized by analysis of the lanthanide - induced NMR shifts.[3]

Dimethyl *trans* - 1 - methylcyclopropane - 1,2 - dicarboxylate is also prepared by the method of McCoy,[11] from *a*-chloropropionate and methyl acrylate according to the procedure described previously[3] for dimethyl *trans* - cyclopropane - 1,2 - dicarboxylate. Condensation in the presence of $NaOCH_3$ in DMSO yields a product mixture containing 80% of the *trans* - dimethyl ester along with 10% each of the *cis*-isomer and an unidentified product. To obtain the *trans*-dinitrile, the total product is hydrolyzed with aqueous KOH to pure *trans*-diacid, which is recovered by crystallization from CH_3CN, and transformed to *trans*-diamide by way of the diacid chloride. Dehydration of the diamide affords the *trans*-dinitrile.

Dimethyl *cis* - 1 - methyl - cyclopropane - 1,2 - dicarboxylate is prepared according to the procedure of McCoy[11] and identified by hydrolysis to a diacid, m.p. 140.8–141.4°. Conversion to the anhydride, reaction with methanol to a mixture of half esters, which is transformed to diester by trreatment with ethereal diazomethane, affords the *cis*-diester. Transformation to the dinitrile is effected by dehydration of the corresponding diamide. *cis*-Dinitrile can be obtained more conveniently by glc separation from a 49.3:50.7 mixture of the *cis* and *trans* isomers prepared by equilibration of the *trans*-isomer by potassium t-butylate in DMSO at 25°.



trans-I *cis*-I

The kinetics of the thermal diastereomerization of *trans*- and *cis*-I in 2% solutions in naphthalene are measured at the boiling point of naphthalene (217.8°), quinoline (237°), tetralin (208°) and phenyl ether (258.1°). Analysis of the product is effected on an OV-225 capillary column programmed from 120 to 155° owing to the large difference in the retention time of the *trans*- and the *cis*-dinitriles. The kinetic data are given in Table 1. Specific rate constants are calculated from the usual expression for reversible first-order reactions and are listed in Table 2 along with activation parameters obtained from these constants by the method of least squares.

The equilibrium constant, K = [*cis*]/[*trans*] = 0.547, is determined at 258° from the equilibrium composition consisting of 64.6:35.4 parts of *trans*-I and *cis*-I, respectively. As the rate constants are measured in both directions, it is not necessary (nor is it convenient due to the slow reaction al lower temperatures) to determine the value of the equilibrium constant experimentally at each temperature. It emerges when the slope of the lines obtained by plotting $-\log(AK\text{-}B)/(A_0K\text{-}B_0)$ vs t, starting with both *cis*- and *trans*-dinitriles, are matched by iterative refinement according to the procedure described previously.[3]

Rate constants are also determined in the gas-phase at two temperatures, 217.8° ± 0.2° and 259.5° ± 0.2°, at a pressure calculated to lie between 100–110 mm. The runs

Table 1. Kinetic data for geometric isomerization of *trans*- and *cis* - 1,2 - dicyanocyclopropane in naphthalene solution

Temp (°C)	Time (hr)	*Cis*-1 (%)[a]	*Trans*-1 (%)[b]
208.0	72.0	3.23	5.09
	144.0	6.67	10.42
	216.0	9.90	15.28
	288.0	12.40	19.87
	384.0	15.66	24.99
217.9	36.0	4.53	6.83
	72.0	8.66	13.26
	108.0	12.85	19.00
	144.0	15.79	25.05
	183.0	18.42	29.32
237.0	8.0	5.78	9.04
	16.0	10.74	17.47
	24.0	15.90	25.32
	32.0	18.60	31.25
	40.0	22.28	36.29
	48.0	24.37	40.37
258.1	2.0	8.36	14.70
	4.0	16.07	26.10
	6.0	21.10	35.72
	8.0	24.80	42.20
	10.0	27.56	47.43

[a] The percent conversion of *trans*-1 to *cis*-1 (ratio of *cis*-1 to the sum of *cis*- and *trans*-1 times 100) is determined by glpc analysis, and is the mean of two or more analyses. The reproducibility is better than 0.2% in most cases.

[b] Starting from *cis*-1.

Table 2. First-order rate constants and activation parameters for geometric isomerization of *cis*- and trans - 1,2 - dicyanocyclopropane

Temp (°C)	$10^6 (k_{t,c} + k_{c,t})$ sec^{-1}	$10^6 k_{t,c}$ sec^{-1}	$10^6 k_{c,t}$ sec^{-1}	$\frac{k_{t,c}}{k_{c,t}}$
208.0	0.3810 ± 0.0045[a] 0.3810 ± 0.0049[b]	0.147	0.234	0.626
217.9	1.0010 ± 0.0198[a] 1.0007 ± 0.0193[b]	0.386	0.614	0.629
237.0	6.129 ± 0.111[a] 6.129 ± 0.058[b]	2.314	3.815	0.607
258.1	38.740 ± 0.336[a] 38.737 ± 0.557[b]	14.27	24.47	0.583[d]
	$\log (k_{t,c} + k_{c,t})$	= (14.91 ± 0.06)	−	(46.95 ± 0.13)/θ[c]
	$\log k_{t,c}$	= (14.24 ± 0.05)	−	(46.40 ± 0.11)/θ[c]
	$\log k_{c,t}$	= (14.80 ± 0.06)	−	(47.20 ± 0.13)/θ[c]

[a] Values of the slope with *trans*-1,2-dicyanocyclopropane as the starting material; errors are ± σ obtained from the least squares treatment.

[b] Values of the slope with *cis*-1,2-dicyanocyclopropane as the starting material.

[c] $\theta = 4.575 \times 10^{-3}\, T$ (°K).

[d] Least squares linear regression of these data afford the equation, $\log K = 0.062 + 0.470/\theta$[c].

are effected in sealed Pyrex ampoules with benzonitrile as an internal standard. Under these conditions, *cis*- and *trans*-dinitriles are the only detectable products. The data are collected in Tables 3 and 4. The calculated activation parameters (from the kinetic data at two temperatures only) do not differ from those obtained in naphthalene solution (Table 2) within the limit of error for the measurement of activation energies. However, there are significant changes in the equilibrium constants at 217.8° (0.235 vs 0.583) and the rate constants at 258.1° for *cis*-*trans* interconversion ($k_{t,c} = 10.13$ and $k_{c,t} = 43.12$ vs $k_{t,c} = 14.27$ and $k_{c,t} = 24.47 \times 10^{-6}\ \mathrm{sec}^{-1}$) between the reactions in the gas-phase and in naphthalene solution, respectively.

In ampoules of Corning 0120 lead-potash glass, the dinitriles isomerize much faster with irreproducible rates. This phenomenon is probably the result of basic surface catalysis. In the presence of diphenylamine, the reaction is slightly faster, contraindicative of a radical chain component.

The activation parameters for *cis*-*trans* geometrical isomerization of 1,2 - dicyanocyclopropane, $E_a = 47.0$ kcal/mol and log A = 14.91, can be translated in the usual fashion: $\Delta H^{\neq} = 46.0$ kcal/mol and $\Delta S^{\neq} = 6.6$ e.u. (at 242.76°). The corresponding parameters for 1,2 - dideuteriocyclopropane[12] are $\Delta H^{\neq} = 63.8$ kcal/mol and $\Delta S^{\neq} = 13.0$ e.u. at 391.38°, whence a value for cyano delocalization energy can be derived: $\mathrm{CN(DE)} = 8.9\ \mathrm{kcal/mol} + f(C_{CN}^{sp}H/CpCp^{\bullet})\ [(E_{C_{CN}^{sp}Cp} - E_{C_{CN}^{sp}Cp^{\bullet}}) - (E_{HCp} - E_{HCp^{\bullet}})]$. In this Dewar-Schmeising correction term, the cyano carbon is sp hybridized and noted as C_{CN}^{sp} while Cp refers to the carbon atom of a cyclopropane ring. Although the value of CN(DE) cannot be estimated, the $\Delta\Delta H^{\neq}$ term of about 9 kcal/mol can be compared directly with the $\Delta\Delta H^{\neq}$ terms for the vinyl (16 kcal/mol) and the phenyl group (14 kcal/mol) when acting as substituents on a cyclopropane ring. Because the Dewar-Schmeising terms vary with the nature of the reaction, application of the 9 kcal/mol lowering by cyano in other reactions should be made circumspectly.

Table 3. Kinetic data for geometric isomerization of *trans*- and *cis* - 1,2 - dicyanocyclopropane in the gas-phase

Temp (°C)	Time (min)	Cis-1 (%)[a]	Rec. (%)[c]	Trans-1 (%)[b]	Rec. (%)[c]
259.5	0.0	0.00		0.00	
	60.0	2.99	87.5	16.57	83.9
	120.0	6.04	92.5	31.55	83.2
	225.0	9.10	89.1	47.23	83.2
	360.0	13.09	86.5	54.81	103.8
	4320.0[d]	19.98	81.3	79.97	102.4
217.8	0.0	0.00		0.00	
	2297.0	2.90	98.7	16.35	96.6
	4320.0	5.24		26.64	98.6
	6480.0	7.98	97.0	37.15	96.6
	8640.0			44.45	100.0
	11000.0	10.90		51.35	89.1

[a] Starting from trans-1, the percent conversion to cis-1 (ratio of cis-1 to the sum of cis-1 and trans-1 times 100).

[b] Starting from cis-1.

[c] Recovery based on benzonitrile as standard.

[d] The runs from which the experimental equilibrium constant is determined.

Table 4. First-order rate constants and activation parameters for geometric isomerization of *trans*- and *cis* - 1,2 - dicyanocyclopropane in the gas-phase

Temp (°C)	$10^6 (k_{t,c} + k_{c,t})$ sec^{-1}	$10^6 k_{t,c}$ sec^{-1}	$10^6 k_{c,t}$ sec^{-1}	$\frac{k_{t,c}}{k_{c,t}}$
259.5 ± 0.2°	53.269 ± 2.17 53.247 ± 5.05	10.13	43.12	0.235
217.8 ± 0.2°	1.480 ± 0.05 1.480 ± 0.02	0.26	1.22	0.215

$$\log (k_{t,c} + k_{c,t}) = 14.05 - 44.65/\theta$$

$$\log k_{t,c} \quad 13.73 - 45.64/\theta$$

$$\log k_{c,t} = 13.86 - 44.43/\theta$$

In order to ascertain the effect of a methyl group on the activation parameters of the rearrangement, a kinetic determination is carried out at 259.5° in 1% solutions in t-butylbenzene of 1 : 1 mixtures of *trans* - 1,2 - dicyano - (*trans* - I) and *trans* - 1 - methyl - 1,2 - dicyanocyclopropanes (*trans*-II) and of similar mixtures of the two *cis*-dinitriles (adamantyl nitrile as an internal standard). A direct comparison of the extent of isomerization of the two dinitriles is determined by glpc analyses of the four-component mixtures at various time intervals (Table 5). The total recovery based on adamantyl nitrile is consistently above 99%. On heating over much longer time intervals (62 hr) at 259.5° equilibrium ratios (K = *cis*/*trans*) are obtained for I (0.41) and II (0.347). Specific rate constants calculated from the data in Table 5 are given in Table 6.

From the ratios of the rates given in Table 6, $\Delta\Delta G^{\neq}$ (259.5°) is 1.98 kcal/mol based on $k_{t,c}$ and 1.95 kcal/mol based on $k_{c,t}$. On the assumption of identical entropies of activation, $\Delta\Delta H^{\neq}$ may be set equal to $\Delta\Delta G^{\neq}$. The lowering of 2.0 kcal/mol in enthalpy of activation can then be compared with the effect of a methyl group on the ease of breaking an sp^2–sp^3 carbon–carbon bond (~ 2.7 kcal/mol per methyl group).

Two features about the *cis*–*trans* equilibrium constants are noteworthy. One is the near identity in t-butylbenzene solution of the equilibrium constants of I and II. Their ratio, $(K_I/K_{II})_{259.5°} = 0.410/0.347$, corresponds to a free energy difference of -177 kcal/mol. The equality in steric size of the hydrogen atom and the cyano group (in the direction perpendicular to its long axis) finds further confirmation in this observation. The other feature is the change in K_I occasioned by transfer from naphthalene to the gas-phase. At 217.8°, $K_I = 0.215$ (gas-phase) and 0.623 (naphthalene; evaluated from the regression line of the data in Table 2). In the gas-phase, *cis*-I is thus disfavored over solution in naphthalene by 1.04 kcal/mol. It is reasonable to ascribe this disfavoring to the complete lack of attenuation by solvent of the energy-raising dipole-dipole interaction. The existence of this dipolar effect is further indicated by the much longer retention time of *cis*-I on the Carbowax column. In this connection, t-butylbenzene is intermediate in effectiveness: $K_I = 0.410$ (0.242 in the gas-phase; 0.547 in naphthalene), all at 259.5°.

Returning to the radical-stabilizing effect of nitrile, we are pleased to quote the directly relatable datum provided by the investigations of Willcott, Rathburn and Cooke.[33] "These workers have examined the *cis*–*trans* isomerization of 1 -cyano - 2 - vinylcyclopropane. Their analysis neglects both the much slower formation of 4-cyanocyclopentene and uncharacterized side reactions. Under static conditions in the temperature range 220–243°, the rate constant for equilibration is given by $(k_{c,t} + k_{t,c}) = 10^{14.1\pm0.3}\ \exp(-41{,}000 \pm 600/RT)\ \text{sec}^{-1}$. In a

Table 5. Kinetic data for geometric isomerization of 1 - methyl - 1,2 - dicyanocyclopropane (*cis* - II and *trans* - II) and 1,2 - dicyanocyclopropane (*cis* - I and *trans* - I) in t-butylbenzene at 259.5° ± 0.2°

Run	Time min.	Trans-II %	Trans-I %	Cis-II %	Cis-I %	Recovery[a] %
1	0.0	0.00	0.00	100.00	100.00	
	60.0	48.65	10.14	51.35	89.86	101.0
	90.0	58.97	14.62	41.03	85.38	100.6
	120.0	65.24	19.00	34.76	81.00	101.0
	240.0	73.65	34.44	26.35	65.56	100.3
	360.0		46.03		53.97	
	480.0		55.32		44.68	
	3720.0	74.22	70.90	25.78	29.10	101.5
2	0.0	100.00	100.00	0.00	0.00	
	60.0	83.50	95.96	16.50	4.04	100.0
	90.0	79.53	93.97	20.47	6.03	100.0
	120.0	76.22	91.68	23.78	8.32	100.1
	240.0	73.78	85.93	26.22	14.07	99.7
	360.0		83.25		16.75	
	480.0		80.51		19.49	

[a] The recovery in % is determined with reference to 1-cyanoadamantane as standard.

Table 6. First-order rate constants for geometric isomerization of 1,2 - dicyanocyclopropane (*trans* I and *cis*-I) and 1,2 - dicyano - 1 - methyl - cyclopropane (*trans*-II and *cis*-II) in t-butylbenzene at 259.5 ± 0.2°

Starting Material	$10^5\ (k_{t,c} + k_{c,t})$ sec^{-1}	$10^5\ k_{t,c}$ sec^{-1}	$10^5\ k_{c,t}$ sec^{-1}	$\frac{k_{t,c}}{k_{c,t}}$
trans-I	4.778 ± 0.147	1.25	3.53	0.353
cis-I	4.774 ± 0.111			
trans-II	30.479 ± 2.490	8.09	22.35	0.362
cis-II	30.403 ± 0.218			

stirred-flow reactor over the temperature range 210–258°, this expression is $(k_{ct} + k_{tc}) = 10^{14.5\pm0.2}$ exp (−41,100 ± 500/RT) sec^{-1}. The causes of the experimental differences leading to somewhat faster reaction as measured under stirred-slow conditions have not been identified. Willcott and Cargle have studied the *cis–trans* isomerization of 2 - deuterio - vinylcyclopropane.[25] Under static conditions in the temperature range 227–325°, the rate constant for equilibration is given by $(k_{ct} + k_{tc}) = 10^{14.5\pm0.1}$ exp (−48,200 ± 1600/RT) sec^{-1}. A comparison reveals that ring substitution of a cyano group lowers the activation energy for *cis–trans* isomerization of vinylcyclopropane by 7.2 ± 1.7 kcal/mol[33]. Translation into $\Delta\Delta H^{\neq}$ leaves this value essentially unchanged: CN(DE) = 7.0 kcal/mol + $f(C^{\ast}_{CN}H/CpCp^{\bullet})$.

A comparison can again be made with 1,2 - dideuteriocyclopropane ($\Delta H^{\neq}$ = 63.7 kcal/mol), whence the combined effect of one cyano group and one vinyl group is 23.7 kcal/mol. If the lowering by the vinyl group derived from the three studies of divinylcyclopropanes mentioned above, ADE = $\overline{16.1}$ + $f(C'H/CpCp^{\bullet})$ is subtracted, there remains for the effect on $\Delta H^{\neq}$ of the cyano group in the cyclopropane isomerization, CN(DE) = 7.6 + $f(C^{\ast}_{CN}H/CpCp^{\bullet})$.

Other estimates in the literature of the effect of a cyano group have been derived from the kinetics of *cis–trans* isomerization of 2 - cyano - 2 - butene[34] and β - cyanostyrene,[35] the decomposition of ethyl and t-butyl nitriles,[36] the gas-phase unimolecular isomerization of cyclopropylcyanide[37] and the gas-phase thermolysis of cyano - substituted cyclobutanes.[38,39]

The observed activation energy, E_a, for the *cis–trans* interconversion of crotonitrile is reported to be 51.3 ± 3.7 kcal/mol (log A = 11.0 ± 1.0),[34] but Benson questions the low A-factor and has recalculated E_a using log A = 12.7 to obtain the value 56.7 kcal/mol.[40] Comparison of the calculated enthalpy of activation, $\Delta H^{\neq}$ = 49.9 kcal/mol, with that for propylene ($\Delta H^{\neq}$ = 60.8 kcal/mol)[41] gives 10.9 ± 3.7 kcal/mol for the lowering of enthalpy of activation.†

cis - β - Cyanostyrene isomerizes to the *trans*-isomer at 610°K: E_a = 46 kcal/mol (log A = 11.6). The corresponding $\Delta H^{\neq}$ is 18.7 kcal/mol lower than that for ethylene (63.4 kcal/mol).[42] While corrections for the conjugative interaction of the nitrile group (3.59 kcal)‡ and of the phenyl group might be made, what is needed is the heat of hydrogenation (or a similar measurement) on β-cyanostyrene and an acceptable value for BDE, if an estimate of the stabilizing effect of CN is to be made.

The activation parameters of the decomposition (rates based on methane formation) of ethyl- and t-butylcyanide and cumyl cyanide have been determined: E_a = 72.7 (log A = 14.1), 70.2 (log A = 15.2) and 54.1 kcal/mol (log A = 12.3), respectively.[36] Heats of formation of the radicals, $\overset{\bullet}{C}H_2CN$ and $(CH_3)_2\overset{\bullet}{C}CN$, are 51.1 ± 3 and 33.8 ± 3 kcal[36] (36.7 kcal),[15] respectively. Values for the stabilization due to CN are estimated to be 12.67 and 10.52 kcal/mol.[17] These higher estimates for the effect of CN may be ascribed to the complications of surface effects, fall-off and free-radical chain reactions.[37] The measured activation energy for the decomposition of cumyl cyanide to $\overset{\bullet}{C}H_3$ and φ–$\overset{\bullet}{C}(CH_3)CN$ radicals is 54.1 kcal/mol (log A = 12.3),[15] whence a stabilization energy due to the combined effect of φ and CN of 31.2 kcal/mol can be estimated (taking the bond dissociation energy of propane to be 85.3 kcal/mol).

A recent experimental evaluation of the delocalization energy of the cyanomethyl radical is obtained by Sarner, Gale, Hall and Richmond[38] from the gas-phase thermolysis of cyclobutanecarbonitrile (758°K), 1,2 - cyclobutanedicarbonitrile (638°K), and 3 - methylenecyclobutanecarbonitrile (748°K). Experimental energies of activation of 56.7 (log A = 15.5), 41.2 (log A = 12.3), and 49.1 kcal/mol (log A = 12.7), respectively, may be compared with that for pyrolysis at 730°K of cyclobutane (E_a = 62.5 kcal/mol, log A = 15.6)[44] and that for the pyrolysis of methylenecyclobutane (E_a = 61.3 kcal/mol, log A = 15.09).[7] From the resultant lowerings of $\Delta\Delta H^{\neq}$ of 5.8, 21.3 and 12.2 kcal/mol, respectively, values for CN(DE) = 5.8, 10.7 and 12.2 kcal/mol + $f(C^{\ast}_{CN}H/C_BC_B^{\bullet})$ are obtained.

Quite recently, King and Godard[19] have restudied the pyrolysis of cyanocyclobutane at very low pressure and confirmed the results of Sarner *et al.*[38] They suggest that a consistent value of the higher pressure limit can also be based on the higher value for the activation energy of cyclobutane cleavage indicated by the low pressure kinetics of Beadle *et al.*[45] In that case, a stabilization energy of 6.4 kcal/mol emerges.

Kinetic studies on the gas-phase unimolecular isomerization of cyclopropylcyanide to cyanopropenes at 660–760° and 2–89 torr, by Luckraft and Robinson[37] provide a value of 7.7 kcal/mol for the stabilization of the radical center by CN *vis-à-vis* H, the difference between the enthalpy of activation, 56.4 kcal/mol, and that for the isomerization of cyclopropane to propene ($\Delta H^{\neq}$ = 64.1 kcal/mol, E_a = 65.6 at 760°K).[46]

The several values in the literature for the stabilizing effect of the cyano group are summarized in Table 7. The values derived from reactions of cyanocyclopropanes are in good agreement with each other. At the moment, an average value of 8 ± 1 kcal/mol seems to be acceptable for the stabilizing effect of the cyano group *vis-à-vis* hydrogen.

Incidental to the evaluation of the effect of a methyl group on the kinetics of *cis–trans* isomerization, *trans* - 1,2 - dicyano - 1 - methylcyclopropane has been prepared in optically active form in order to determine whether the presence of the fully substituted carbon atom significantly alters the relative rotational propensity. The exceptional preference of the benzylic carbon atom in ethyl 1,2 - diphenylcyclopropane - 1 - carboxylate to rotate (R_A = 13.3) gives heightened interest to this question.[47]

Resolution is effected on the *trans*-dicarboxylic acid by means of quinine. Conversion to (−)-*trans*-II is achieved in the manner previously described: a sample heated in benzene solution at 230 ± 2° for 38,700 sec affords recovered (−)-*trans*-II with 0.696 of the original optical activity.

Recovered *cis*-II is 0.15 of optical purity and has the positive sign of rotation corresponding to an excess of the C_2 enantiomorph. The product has thus resulted 58% by

---

† From thermodynamic parameters of *cis*- and *trans*-crotonitrile, ΔH = 0.17 ± 0.12 kcal and ΔS = −0.39 ± 0.19 kcal/mol S, the *cis* isomer is more stable than the *trans* due to higher entropy.

‡ $\Delta H_f^\circ(g)CH_3CH_2$–CN is +8.12 kcal,[43a] and $\Delta H_f^\circ(g)CH_3$–CH_3 is −20.24 kcal. The difference +28.36 kcal when compared to the difference (+31.95) between the heat of formation of CH_2=CH–CN, $\Delta H_f^\circ(g)$ = +44.1[43a] and of ethylene, $\Delta H_f^\circ(g)$ = +12.15 kcal, results in a value of +3.59 kcal (+31.95 − [+28.36]) for CN vs H conjugative interaction.

Table 7. Summary of stabilizing effects of the cyano group in various reactions

Reaction Type	Stabilization (kcal/mole)	Dewar-Schmeising Term	References
Olefin isom.	10.9 ± 3.7	$f(C^{\bullet}_{CN}H/C'C'\bullet)$	34, 35, 40
C–C cleavage	11.6 ± 1.6	$f(C^{\bullet}_{CN}H/CC\bullet)$	36, 37
Cyclobutane decomp.	9.6 ± 3.4	$f(C^{\bullet}_{CN}H/C_BC_B\bullet)$	38
Cyclobutane decomp.	6.4	"	39, 45
Cyclopropane rearr.	7.7	$f(C^{\bullet}_{CN}H/CpCp\bullet)$	37
Cyclopropane isom.	7.2 ± 1.7	"	33
Cyclopropane isom.	8.9 ± 1.0	"	this work

rotation of the cyano-hydrogen carbon and 42% by rotation of the cyanomethyl carbon atom. Their ratio represents a minimum value for the rotational propensity of the less highly substituted carbon atom: $R_A \geq 1.37$. Even though this value obtained from a single experiment would be increased by extrapolation to zero time, it may be concluded that the resistance to rotation of the disubstituted carbon atom is much smaller than it is in the case of Chmurny and Cram.[45]

EXPERIMENTAL

General. NMR spectra are recorded on Varian A-60 and T-60 spectrometers. IR spectra are determined on a Perkin-Elmer Model 337 grating spectrophotometer. Glpc analyses are performed on a Perkin-Elmer Model 990 Gas Chromatograph using a Perkin-Elmer OV-225 capillary column, 600 by 0.02 in. (Column A). The areas of peaks are obtained with a Digital Autolab Model 6300-01 Integrator. Purification of samples is accomplished by preparative glpc on Autoprep Model A-700 using Column B (60 × 0.25 in.; 20% SE-30 on Anakrom AB) and Column C (162 × 0.25 in.; 10% Carbowax 20 M on Anakrom ABS). Mass spectral analyses are made with an AEI Model MS9 double-focussing mass spectrometer.

M.ps and b.ps are uncorrected.

trans - *Cyclopropane - 1,2 - dicarboxamide.* Dimethyl *trans* - cyclopropane - 1,2 - dicarboxylate (1.1 g), prepared according to the procedure described earlier,[1] was stirred with 20 ml of 30% aqueous ammonium hydroxide in a tightly stoppered bottle at 27°. The diester dissolved within 1 hr and was replaced by a crystalline solid. After the contents had been stirred for an additional 3 hr, the crystals were collected, washed with anhyd MeOH and dried *in vacuo*: 0.75 g (84%), m.p. 275–280°; NMR (D_2O) δ 1.05–1.3 (2H, m), 1.83–2.1 (2H, m), 4.6 (s, HDO).

cis - *Cyclopropane - 1,2 - dicarboxamide*: *cis* - Dimethyl ester (1.1 g),[1] treated according to the procedure described for the *trans* isomer, afforded *cis*-diamide in 80% yield as a colorless solid; m.p. 230°; NMR (D_2O) δ 1.23–1.68 (2H, m), 2.11–2.40 (2H, m), 4.86 (s, HDO).

trans - 1,2 - *Dicyanocyclopropane* (trans - 1). To a suspension of *trans* - diamide (1.28 g, 10 mmol) in 15 ml of dry benzene in a 25 ml flask with a side-arm closed with a serum cap and swept with a slow stream of dry N_2, 1.5 ml (21 mmol) of thionyl chloride was introduced with a syringe through the serum cap followed by dropwise addition of 2 ml (21 mmol) of DMF at 25°. Within 15 min the solid dissolved and two layers were formed. The mixture was stirred for 4 hr at 25–30°, poured over crushed ice and extracted with three 25 ml portions benzene. The combined extracts were washed with dil $NaHCO_3$ aq and then with water, and dried ($MgSO_4$). Removal of benzene on a rotary evaporator gave 0.6 g (65%) colorless crystals, m.p. 70–72°; after one crystallization from petroleum ether—CH_2Cl_2, m.p. 72.5–73°; NMR ($CDCl_3$) δ 1.47–1.75 (complex m, 2H), 2.0–2.3 (complex m, 2H); IR ($CHCl_3$): 3110 (w), 3050, 3010 (m), 2250 (s), 1445 (w), 1215 (s), 1070, 1055, 988, 910, 865, 720, 680 (m) cm^{-1}.

cis - 1,2 - *Dicyanocyclopropane* (cis - 1). Following the procedure described above for the *trans*-dinitrile, *cis*-diamide (2.56 g, 20 mmol) in 30 ml benzene was treated with 3 ml (42 mmol) thionyl chloride and 4 ml DMF at 25° and stirred for 9 hr. Dilution with 30 ml ice-water, separation of the benzene layer, extraction of the aqueous portion with three 20 ml portions of CH_2Cl_2 yielded a combined benzene and CH_2Cl_2 extract which was washed with two 20 ml portions water, dil $NaHCO_3$ aq, and with sat NaCl aq. The dried extracts were concentrated on a rotary evaporator to afford 0.96 g, m.p. 54–58°. One crystallization from pet-ether-CH_2Cl_2 gave colorless crystals, m.p. 59–60°; NMR ($CDCl_3$) δ 1.47–1.73 (complex m, 2H), 1.95–2.23 (complex m, 2H); IR ($CHCl_3$): 3070 (w), 3020, 2980 (m), 2240 (s), 1455, 1375 (m), 1220 (s), 1130, 1070, 955, 850, 725, 680 (m) cm^{-1}.

Dimethyl trans - 1 - *methylcyclopropane - 1,2 - dicarboxylate.* This compound was prepared according to the procedure described previously[1] for dimethyl *trans* - cyclopropane - 1,2 - dicarboxylate. To a well-stirred soln of methyl 2 - chloropropionate (25.5 g, 0.21 mol) and methyl acrylate (45 g, excess), NaOMe (Fisher, 11.8 g, 0.21 mol) was added in small portions at 40–60° under N_2. After the addition was complete, the mixture was stirred for an additional 3 hr. Addition of 100 ml water and extraction with three 50 ml portions ether, washing with two 10 ml portions water, drying over $MgSO_4$ and distillation gave a fraction (22 g) of b.p. 50–60°(8 mm) and a second fraction (26.8 g) of b.p. 77–82° (5.2 mm) and a third fraction (4.5 g) of b.p. 83–95° (5 mm). Combined higher boiling fractions (31.3 g) correspond to 85% yield of the product based on methyl 2 - chloropropionate. The second fraction was redistilled and gave a major fraction, b.p. 94–95° (6 mm) which showed three peaks on Column C at 165°, in the ratio 80:10:10 with retention times of 33, 40 and 46 min, respectively. These were collected by preparative glpc using the same column. From the NMR spectra of the purified fractions and from the experiments described below, the major peak (r.t., 33 min) was assigned to dimethyl *trans* - 1 - methylcyclopropane - 1,2 - dicarboxylate: NMR ($CDCl_3$) δ 1.23–1.7 (complex m with an overlapping singlet due to $-CH_3$ at 1.4, 5H); 2.23–2.48 (pair of d, 1H); 3.7 (s, 6H). The minor peak (r.t., 40 min) was assigned to the *cis*-dimethyl ester and the third peak (r.t., 46 min) was unidentified (no cyclopropyl protons in the NMR).

Dimethyl cis - 1 - *methylcyclopropane* - 1,2 - *dicarboxylate.* This substance was prepared from methyl acrylate (6.9 g, 0.08 mol), methyl 2 - chloropropionate (4.9 g, 0.04 mol) and NaOMe (2.3 g, 0.042 mol) at 15–35° according to the procedure of McCoy.[11] After removal of a lower boiling fraction, distillation afforded a fraction of b.p. 82–95° (5 mm) which, on glpc analysis on Column C at 165°, gave the same three peaks as observed in the preparation of the *trans* isomer but in this case the 40 min peak assigned to the *cis* isomer was the major component of the product mixture. A sample of pure *cis*-dimethyl ester was obtain by preparative glpc on the same column. NMR ($CDCl_3$) δ 0.91–1.3 (m, 1 H), 1.4 (s, 3 H), 1.68–1.87 (m, 2H) and 3.67 (s, 6 H).

To confirm the identity of this material, the product mixture (3.5 g) was hydrolyzed with 25 ml of 15% KOH aq at 70–80° for 5 hr. A work-up procedure similar to that used for the preparation of the *trans* isomer gave 2.4 g of a crystalline solid, which yielded pure *cis*-diacid, m.p. 140.8–141.4° after recrystallization from MeCN. The remainder of the product was heated with 2.5 ml Ac_2O at 80–100° for 30 min. Removal of excess Ac_2O and AcOH under reduced pressure gave a residue, sublimation of which at 80° (6 mm) yielded 1.07 g of the anhydride, m.p. 46–47°, NMR ($CDCl_3$) δ 1.41–2.17 (complex m with overlapping singlet at 1.57 due to $-CH_3$, 5H), 2.48–2.68 (pair of d, 1H).

Reaction of the anhydride (1.05 g) with 15 ml MeOH at 70° for 1 hr gave a mixture of half-esters, treatment of which with diazomethane in ether at 0° afforded 1.1 g of dimethyl *cis* - 1 - methylcyclopropane - 1,2 - dicarboxylate. NMR spectrum of this sample of the *cis*-diester was indistinguishable from that of a sample obtained by preparative glpc of a sample obtained by preparative glpc of the original product mixture (see above).

trans - 1 - *Methylcyclopropane* - 1,2 - *dicarboxylic acid.* A mixture (18.2 g) containing 80% of dimethyl *trans* - 1 - methylcyclopropane - 1,2 - dicarboxylate and 10% each of the *cis* isomer and an unidentified product, was treated with 100 ml of 17% KOH aq for 6 hr at 80–90° and concentrated on the rotary evaporator to a residue which was cooled in ice and acidified with conc HCl. Extraction of the product with five 60 ml portions of ether gave 16.1 g of colorless solid; recrystallization from MeCN afforded 14.7 g of crystalline solid, m.p. 171.4–172°.

trans - 1 - *Methylcyclopropane* - 1,2 - *dicarboxamide.* The corresponding cyclopropane dicarboxylic acid (2.1 g) was heated with thionyl chloride (20 ml) at 70–80° for 2 hr. Removal of excess thionyl chloride under reduced pressure afforded the diacid chloride which was dissolved in CH_2Cl_2 (20 ml) and treated with NH_3 soln in CH_2Cl_2 at 0°. The precipitated solids were isolated by filtration, dissolved in a minimum volume of MeOH and diluted with ethanol-diethyl ether (1 : 4) to precipitate NH_4Cl. The filtrate was concentrated on a rotary evaporator to a residue which was crystallized from 30 ml of EtOH : 1.5 g; m.p. 182–183°; NMR (D_2O) δ 0.93–1.4 (complex m with overlapping singlet at 1.16, 5H), 1.97–2.25 (m, 1H), 4.53 (HDO).

trans - 1 - *Methyl* - 1,2 - *dicyanocyclopropane.* To the suspension of the above diamide (0.98 g, 6.9 mmol) in benzene (8 ml) was added thionyl chlorine (1.0 ml) and DMF (1.4 ml) at 28° under N_2. After stirring for 4 hr, the mixture was diluted with 10 ml water and extracted with 20 ml benzene and three 20 ml portions CH_2Cl_2. The combined extracts were washed with water, dil $NaHCO_3$ aq, water, dried over $MgSO_4$ and concentrated under reduced pressure to furnish 0.61 g (83%) crude product. Glpc analysis on Column A at 120° showed one major peak. Purification on Column B at 145° gave a colorless liquid: NMR ($CDCl_3$) δ 1.23–1.90 (complex m with overlapping s at 1.63 due to $-CH_3$, 5H), 2.1–2.37 (pair of d, 1H); IR ($CHCl_3$): 3050, 2980, 2940 (w), 2240 (s), 1460, 1440, 1375 (m), 1083, 970, 915 (m) cm^{-1}.

cis - 1 - *Methyl* - 1,2 - *dicyanocyclopropane.* A sample of the unpurified, crude *trans*-dinitrile (0.55 g) was equilibrated in DMSO (3 ml) containing potassium t-butylate (50 mg) for 5 min at 25°. Dilution with 10 ml water and extraction with four 20 ml portions ether afforded an ether extract which was washed with water, dried over $MgSO_4$ and concentrated under reduced pressure to afford 0.34 g of a colorless liquid. Glpc analysis on Column A at 120° revealed two peaks of ret. times of 8 and 44 min in the ratio 50.7 : 49.3 corresponding to *trans* - and *cis* - 1 - methyl - 1,2 - dicyanocyclopropane, respectively. Separation and purification was effected on Column B at 140° (helium flow 60 ml/min) yielding samples of the *trans* - and the *cis*-dinitrile. After a second chromatograph on the same column, glpc analysis on Column A revealed *trans*-dinitrile of 100% purity and *cis*-dinitrile contaminated by 0.1% of the *trans*-isomer. The NMR spectrum of the *trans*-dinitrile was identical to that of starting material while the NMR spectrum of the *cis*-dinitrile in $CDCl_3$ showed a complex multiplet at δ 1.38–1.83 with an overlapping singlet at δ 1.5 due to $-CH_3$ and IR ($CHCl_3$): 3100 (w), 3010 (m), 3475, 3430 (w), 2240 (s), 1450, 1430, 1375 (m), 1090, 1065 (w), 980 (m), 900 (w).

The *cis*-dinitrile could also be prepared in low yield by the dehydration of the corresponding diamide with $SOCl_2$–DMF according to the procedure described for the *trans*-isomer. The *cis*-diamide, prepared from dimethyl *cis* - 1 - methyl - 1,2 - cyclopropane dicarboxylate by treatment with 30% NH_4OH for 14 hr in 30% yield could be crystallized from EtOH–MeOH (2 : 1) at 0°: m.p. 200–202°.

Resolution of trans - 1 - *methylcyclopropane* - 1,2 - *dicarboxylic acid.* A soln of the *trans*-diacid (0.72 g, 5 mmol) and quinine (3.24 g, 10 mmol) in 1 : 2 EtOH–EtOAc (25 ml) yielded 1.4 g of crystalline salt after being stored at 27° for 3 days. Diacid was recovered from 0.15 g of this salt by suspension in water, acidification with cold 20% HCl, extraction with ether and concentration: $[\alpha]_D^{28}$ + 91.5° (*c*, 0.699, EtOH). Two recrystallizations of 1.2 g of this salt from the same solvent furnished 0.5 g of salt, m.p. 203–204°; diacid: $[\alpha]_D^{28}$ + 163.5° (*c*, 0.8312, EtOH). The mother liquors yielded a second crop (0.95 g). The filtrate when concentrated yielded a residue (1.1 g) which, on hydrolysis, furnished 0.15 g of the diacid: $[\alpha]_D^{28}$ - 65.7° (*c*, 1.238, EtOH).

(-) - trans - 1 - *Methylcyclopropane* - 1,2 - *dicarboxamide.* Partially resolved (−) - diacid, 0.14 g ($[\alpha]_D^{27}$ − 65.7°) was treated with thionyl chloride (1 ml) for 2 hr at 50–60°. A work-up procedure similar to that used for racemic material gave 0.18 g of crystalline solid, m.p. 182–183°.

( ) - trans - 1 - *Methyl* - 1,2 - *dicyanocyclopropane.* The product of dehydration of the above diamide (0.18 g) with $SOCl_2$–DMF according to the procedure described for the preparation of racemic dinitrile was purified by preparative glpc on Column B at 120° to afford 70 mg of a sample of ( ) - *trans* - II, $[\alpha]_{546}^{22}$ - 245.7° (*c*, 0.2373, abs EtOH).

Kinetics of geometric isomerization of cis- *and* trans - 1,2 - *dicyanocyclopropanes*

(a) *In naphthalene solution.* Rates were determined in 2% soln in naphthalene, degassed and sealed under vacuum in Pyrex ampoules. Details of the procedure employed and description of the kinetic bath have been given previously.[1] An estimate of the total recovery of these isomerizations was obtained in a separate run with mixtures of 1,2 - dicyano- and 1 - methyl - 1,2 - dicyanocyclopropane in t-butylbenzene soln using adamantyl nitrile as an internal standard (see Table 5). Before use, *cis* - and *trans* - 1,2 - dicyanocyclopropane were purified by crystallization and 1 - methyl - 1,2 - dicyanocyclopropanes were purified by preparative glpc on Column B at 145°. Naphthalene was sublimed prior to use, while t-butylbenzene (99.9% pure) was used as received from Chemical Samples, Co., since a minor impurity did not interfere with the glpc analyses of the mixtures of product.

A stock soln in naphthalene was prepared by dissolving at 90° 40 mg of the dinitrile in 2.00 g of freshly sublimed naphthalene. The solid mass obtained on cooling the soln to room temp. was thoroughly ground in a mortar. About 150–200 mg of this solid was then introduced into Pyrex ampoules (20 × 0.7 cm) which were evacuated and sealed. After being heated for specified times, the samples were dissolved in 1 ml of toluene and analyzed by glpc. No correction for detector response factors was made. The experimental data are given in Table 1.

The rate constants for the reaction and its reverse were obtained by the usual equation for reversible first-order reactions,

$$-\log x = -\log[(AK\text{-}B)/(A_oK\text{-}B_o)] - t(k_{t,c} + k_{c,t})/\ln 10,$$

in which B_o and B were the concentrations of the *cis*-isomer at times zero and t (sec), respectively. The experimental value of the equilibrium constant ($k_{t,c}/k_{c,t}$), determined in both directions by heating for 45 hr at 258°, was 0.547 (35.37:64.63). Optimized, final values for $k_{t,c}$ and $k_{c,t}$ were obtained using a least squares computer program for iterative adjustment of the value of K within narrow limits of its experimental value at 258° until values of the slope for the forward and reverse directions became identical within 1 part in 10,000. The individual rate constants $k_{t,c}$ and $k_{c,t}$ were computed using optimized values of the slope and equilibrium constant (Table 2). The computer derived value at 258.1° of K (0.583) was identical within the expected limits of uncertainty to the experimental value of K (0.547). The Arrhenius activation parameters were obtained from the individual rate constants and the sums of the rate constants at 208°, 217.9°, 237° and 258.1° by the method of least squares. The results are given in Table 2.

(b) *In the gas-phase.* These runs were carried out in the apparatus and in the manner described previously.[3] Samples of the *trans*-I (11.2 mg) and the *cis*-I (11.6 mg) were dissolved in chromatographically pure benzonitrile (25 μl) and the clear liquid decanted in order to separate any undissolved material. Analysis of a soln of the mixture of benzonitrile-dinitrile in benzene (2 μl in 0.2 ml) showed a ratio (70:30 and 71:29 for *trans*-I and *cis*-I, respectively). These ratios were taken as references for calculating the recovery of the product mixture after heating for specified time periods.

For kinetic runs at 217.8° and 259.5°, 2 μl of the stock soln was introduced into 6 ml Pyrex ampoules (calculated to provide a total pressure of 110 mm/Hg at 259°). The samples were degassed, sealed at 10^{-3} mm and heated for specified time intervals. The product was dissolved in benzene and analyzed as described for soln runs. The experimental data are collected in Table 3. On heating over much longer time intervals (3 days) at 259.5°, product composition corresponding to the equilibrium ratio was obtained: 18.98:81.02 and 20.03:79.97 ($k_{t,c}/k_{c,t}$ = 0.234 and 0.250) with *trans*-I and the *cis*-I, respectively, as starting material. In comparison, the value of the equilibrium constant in naphthalene soln at 259.5° was 0.547, corresponding to 35.37:64.63 for the *cis–trans* ratio. With benzonitrile as an internal standard, quantitative estimates of recovery were unsatisfactory because the retention time of benzonitrile was too close to that of the solvent. The experimental data are reported in Table 3. First-order rate constants and activation parameters calculated from these data are summarized in Table 4.

Kinetics of geometric isomerization of mixtures of cis - 1,2 - *dicyano and* cis - 1 - *methyl* - 1,2 - *dicyanocyclopropanes, and of the two* trans - *dinitriles.* A mixture of *cis* - 1,2 - dicyanocyclopropane (6.5 mg), *cis* - 1 - methyl - 1,2 - dicyanocyclopropane (6.3 mg) and 1 - adamantyl nitrile (AdCN) (6.7 mg) was dissolved in t-butylbenzene (0.6 ml) by heating (60°). The soln was cooled to room temp. and transferred to a separate container to remove any undissolved material and analyzed for the initial ratio of the three components, 31.13:27.73:41.14 for *cis*-I, *cis*-II and 1-adamantyl nitrile, respectively. These values differed from the ratios based on weights (33.34:32.31:34.35), since the dinitriles were not as readily soluble in t-butylbenzene as the internal standard, AdCN.

A stock soln of the *trans*-dinitriles was prepared in a similar manner from 6.9 mg of *trans*-I, 5.8 mg of *trans*-II and 6.4 mg AdCN in 0.6 ml of t-butylbenzene. This mixture corresponded to the ratio 36.2:30.4:33.4 while glpc analysis gave 32.38:29.31:38.41, respectively.

For kinetic determination, 0.1 ml of stock solution was heated in 2 ml sealed Pyrex ampoules (calculated to develop a pressure of 16 atm at 259°) for specified time periods. The results of product analyses are collected in Table 5. The percent recovery was based on the glpc analysis of the original solns and not on the weights of the samples. A direct comparison of the rate constants (calculated by the methods described for previous runs) for the two dinitriles under identical conditions is provided in Table 6. Position of equilibrium was determined in both directions and after 62 hr corresponded to a ratio of 29.1:70.9 (K = 0.410) and 25.78:74.22 (K = 0.347) for 1,2-dicyano and 1 - methyl - 1,2 - dicyanocyclopropane, respectively.

In a repeat determination of equilibrium, 1% soln of *cis*-II in t-butylbenzene was heated for 14 hr at 259° in a sealed Pyrex ampoule. From the results of two consecutive analyses of the product, a ratio of 25.25 ± 0.2:74.8 ± 0.2 was obtained.

Thermal isomerization of (−) - trans - II *in benzene solution.* A 6% benzene soln of (−) - *trans* - II ($[\alpha]^{22}_{546}$ − 245.7°) was heated in a tube furnace at 228–232° in a sealed Pyrex ampoule for 10.75 hr. Glpc analysis of the recovered product on Column A at 120° showed two peaks corresponding to a major and a minor component identified by retention time as starting material and the product of its geometric isomerization, *cis*-II, respectively. Separated by preparative glpc using Column B, recovered *trans*-II has $[\alpha]^{22}_{546}$ − 171.11° (*c*, 1.0905, abs EtOH) corresponding to 69.6% retention of optical purity, while *cis*-II, purified by repeated chromatography, had the very low specific rotation of $[\alpha]^{22}_{546}$ + 7.9° (*c*, 0.3415, CH_2Cl_2). This rotation corresponded to 15% retention of optical purity (see below).

In order to determine the rotation of *cis*-II relative to *trans*-II, 20 mg of the above sample of *trans*-II ($[\alpha]^{22}_{546}$ − 171.1°) was subjected to equilibrating conditions (DMSO–KOtBu). Separation by preparative glpc gave two pure fractions: (−) - *trans* - II, $[\alpha]^{22}_{546}$ − 156.8° (*c*, 0.2622, abs EtOH) and (+) - *cis* - II, $[\alpha]^{22}_{546}$ + 36.8° (*c*, 0.2498, abs EtOH). The specific rotation of optically pure (+) - *cis* - II was then estimated to be +52.9°.

Acknowledgement—We wish to express our gratitude to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for their support of this work.

REFERENCES

[1] F.-G. Klärner, *Angew. Chem.* Intern. Ed. **11**, 832 (1972).

[2] W. von E. Doering and L. Birladeanu, *Tetrahedron* **29**, 499 (1973).

[3] W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.* **96**, 1168 (1974).

[4] W. von E. Doering and K. Sachdev, *Ibid.* **97**, 5512 (1975).

[5a] J. K. M. Sanders and D. H. Williams, *Ibid.* 93, 641 (1971); [b] F.-G. Klärner, *Tetrahedron Letters* 3611 (1971); [c] M. R. Willcott, R. E. Lenkinski and R. E. Davis, *J. Am. Chem. Soc.* **94**, 1742 (1972); [d] R. E. Davis and M. R. Willcott, *Ibid.* **94**, 1744 (1972); [e] N. S. Angerman, S. S. Danyluk and T. A. Victor, *Ibid.* **94**, 7137 (1972); [f] R. E. Davis, M. R. Willcott, R. E. Lenkinski, W. von E. Doering and L. Birladeanu, *Ibid.* **95**, 6846 (1973).

[6] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959); *Ibid.* **11**, 96 (1960).

[7] W. von E. Doering and G. H. Beasley, *Ibid.* **29**, 2231 (1973).

[8] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **56**, 638 (1934).

[9] T. W. T. Taylor and A. R. Murray, *J. Chem. Soc.* 2078 (1938).

[10] A. V. Santoro, E. J. Banett and H. W. Hoyer, *J. Am. Chem. Soc.* **89**, 4545 (1967).

[11] R. J. Crawford and T. R. Lynch, *Can. J. Chem.* **46**, 1457 (1968); J. A. Berson and J. M. Balquist, *J. Am. Chem. Soc.* **90**, 7343 (1968); W. L. Carter and R. G. Bergman, *Ibid.* **90**, 7344 (1968); R. G. Bergman and W. L. Carter, *Ibid.* **91**, 7411 (1969).

[12] E. W. Schlag and B. S. Rabinovitch, *Ibid.* **82**, 5996 (1960).

[13] L. B. Rodewald and C. H. DePuy, *Tetrahedron Letters* 2951 (1964).

[14] M. P. Kozina, M. Y. Lukina, N. D. Zubereva, I. L. Safonova, S. M. Skuratov and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR* **138**, 843–845 (1961), Engl. Ed. 537; *Proc. Acad. Sci. USSR, Chem. Sect.* **138**, 537–539 (1961).

[15] H. E. O'Neal and S. W. Benson, *Free Radicals* (Edited by J. K. Kochi), Vol. 2, Chap. 17. Wiley, New York (1973).

[16] S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions.* National Bureau of Standards, 21 (1970), Washington, D.C., provide refs and critical evaluation.

[17] R. Walsh, D. M. Golden and S. W. Benson, *J. Am. Chem. Soc.* **88**, 650 (1966).

[18] G. L. Estaban, J. A. Kerr and A. F. Trotman–Dickenson, *J. Chem. Soc.* 3873 (1963).

[19] A. H. Sehon, M. Szwarc and B. N. Ghosh, *J. Chem. Phys.* **18**, 1142 (1950).

[20] O. Gellner and H. A. Skinner, *J. Chem. Soc.* 1145 (1949).

[21] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, New York (1970).

[22] E. Vogel and R. Sunderman, Ph.D. Dissertation, Köln (1966), ref. 311. in M. R. Willcott, R. L. Cargill and A. B. Sears, *Progress in Physical Organic Chemistry* Vol. 9 (1972).

[23] M. Ari and R. J. Crawford, *Can. J. Chem.* **50**, 2158 (1972).

[24] Unpublished results of W. R. Roth cited in Willcott, Cargill and Sears,[22] p. 67.

[25] M. R. Willcott and V. H. Cargle, *J. Am. Chem. Soc.* **91**, 4310 (1969).

[26] W. R. Roth and J. König, *Ann.* **688**, 28 (1965).

[27] R. J. Ellis and H. M. Frey, *J. Chem. Soc.* 5578 (1964); *Proc. Chem. Soc.* 221 (1964).

[28] M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* **A260**, 424 (1961); *Ibid.* **A257**, 122 (1961).

[29] [a] K. W. Egger, D. M. Golden and S. W. Benson, *J. Am. Chem. Soc.* **86**, 5420 (1964); [b] D. M. Golden, A. S. Rodgers and S. W. Benson, *Ibid.* **88**, 3196 (1966).

[30] W. K. Busfield, K. J. Ivin, H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.* **57**, 1064 (1961).

[31] L. McCoy, *J. Am. Chem. Soc.* **80**, 6568 (1958).

[32] Cf. J. C. Thurman, *Chem. Ind.* 752 (1964); *J. Org. Chem.* **24**, 26 (1959); *Tetrahedron* **19**, 161 (1963).

[33] M. R. Willcott, O. O. Rathburn and R. S. Cooke, privately communicated 8 September 1974 with permission to quote. See Willcott, Cargill and Sears,[22] p. 47.

[34] J. N. Butler and R. D. McAlpine, *Can. J. Chem.* **41**, 2487 (1963).

[35] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **58**, 2428 (1936); *Ibid.* **57**, 269 (1935).

[36] M. Hunt, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.* 5074 (1965).

[37] D. A. Luckraft and P. J. Robinson, *Int. J. Chem. Kin.* **5**, 137 (1973).

[38] S. F. Sarner, D. M. Gale, H. K. Hall and A. B. Richmond, *J. Phys. Chem.* **76**, 2817 (1972).

[39] K. D. King and R. D. Goddard, *Intern. J. Chem. Kin.* **7**, 109 (1975).

[40] S. W. Benson, *Thermochemical Kinetics*. Wiley, New York (1968); and Ref. 16.

[41] M. C. Flowers and N. Jonathan, *J. Chem. Phys.* **50**, 2805 (1969).

[42] J. E. Douglas, B. S. Rabinovitch and F. S. Looney, *Ibid.* **23**, 315 (1955).

[43] [a] K. E. Howlett, *J. Chem. Soc.* 1784 (1955); [b] P. B. Howard and H. A. Skinner, *Ibid.* A, 1536 (1966).

[44] R. W. Carr and W. D. Walters, *J. Phys. Chem.* **67**, 1370 (1963).

[45] P. C. Beadle, D. M. Golden, K. D. King and S. W. Benson, *J. Am. Chem. Soc.* **94**, 2943 (1972).

[46] T. S. Chambers and G. B. Kistiakowsky, *Ibid.* **56**, 399 (1934).

[47] A. B. Chmurny and D. J. Cram, *Ibid.* **95**, 4237 (1973).