Restricted Rotation Involving the Tetrahedral Carbon. XXVII. Rotamers of 9-(1-Cyano or 1-Methoxycarbonyl-1-methylethyl)triptycene Derivatives Carrying a Substituent in 1-Position[1]

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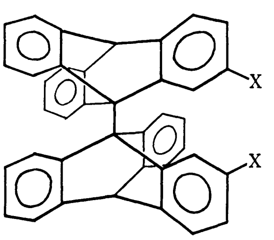
The title compounds were prepared by the reaction between 9-(1-cyano or 1-methoxycarbonyl-1-methylethyl)-anthracene and substituted benzynes and their rotational isomers were isolated. The barriers to rotation of these compounds were found to be 35—36 kcal/mol and 32—34 kcal/mol for the processes *dl*→*meso* and *meso*→*dl*, respectively.

Triptycenes carrying a tertiary carbon in the 9-position are known to exhibit unusually high barriers to rotation about the C_9-C_{subst} bond.[2] Thus various rotational isomers of this type have been isolated. The highest barrier to rotation has been realized with 9,9′-bitriptycyl derivatives (**1**).[3] The second highest barrier known to date is that of 9,10-bis(1-cyano-1-methylethyl)triptycene (**2**).[4] We have felt that it will be interesting to see whether triptycenes carrying a tertiary carbon in 9-position, one of which substituents is an sp^2 or sp hybridized carbon atom, exhibit high barriers to rotation in general. Since the barrier to rotation is the difference in energy between the ground and the transition states, the sp^2 or sp hybridized carbon might fit well in the triptycene skeleton to lower the ground state.



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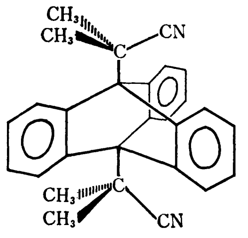

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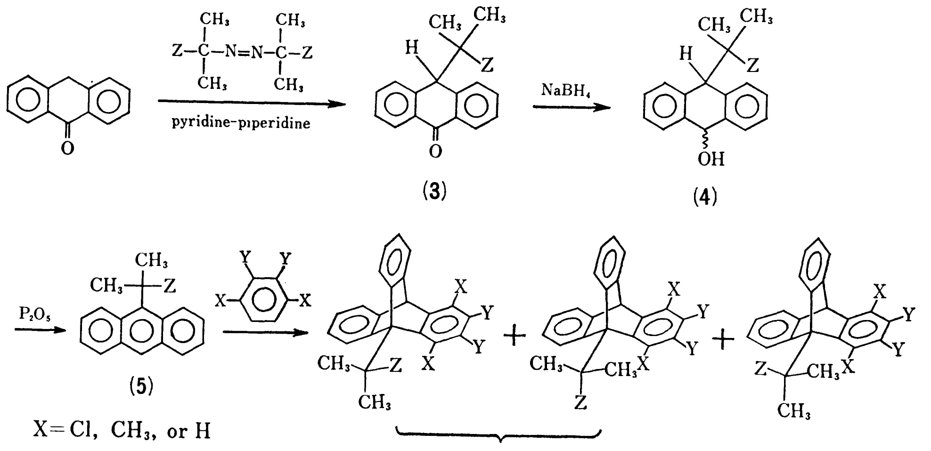
Syntheses

Syntheses of triptycenes are usually carried out by the Diels-Alder reaction of a substituted anthracene with a benzyne. The first problem, therefore, was to synthesize appropriately substituted anthracenes. This posed a problem, because this kind of compounds are usually prepared by the Grignard reaction with anthrone followed by dehydration. The electronegative groups such as cyano and methoxycarbonyl would not survive under the reaction conditions. Literature search indicated that, although there was a method to introduce a tertiary carbon carrying two electronegative groups to the 9-position of anthracene,[5] there was no method to give the desired anthracenes. Various attempts were made, such as Reformatsky reaction, reaction of anthrone with the lithium derivative of isobutyronitrile, and methylation of 9-cyanomethylanthracene, but they all failed probably for steric reasons. Finally we were able to introduce 1-cyano- or 1-methoxycarbonyl-1-methylethyl group to the 10-position of anthrone by allowing the latter to react with azobisisobutyronitrile or dimethyl azobisisobutyrate under basic conditions.[6] The substituted anthrone (**3**) was reduced with sodium borohydride and the product (**4**) was dehydrated with phosphorus pentaoxide. The 9-substituted anthracene (**5**) was treated with benzynes to give desired triptycenes



X= Cl, CH₃, or H
Y= Cl or H
Z= CN or COOCH₃

(*dl*-**6**) (*meso*-**6**)

(**6**). Reactive benzynes such as tetrachlorobenzyne reacted to afford 1,4-addition products in addition to the desired 9,10-adducts. The former was found very difficult to remove from the latter. Thus the olefinic bond of the former was oxidized with performic acid and the resulted oxygenated compounds were removed by chromatography.

Experimental

10-(1-Cyano-1-methylethyl)anthrone (**3**, *Z=CN*). A solution of 3.07 g (15.8 mmol) of anthrone and 6.0 g (37 mmol) of azobisisobutyronitrile in 30 ml of pyridine–piperidine (2: 1) was heated at 90 °C for 6 h with stirring. The mixture was poured into excess of hydrochloric acid after cooling and the precipitate was collected. Tetramethylsuccinonitrile was removed by steam distillation of the precipitate and the residue taken up in dichloromethane. After drying, the solvent was evaporated and the residue was heated in vacuo until no sublimate was observed. The residue was chromatographed on alumina using hexane–benzene as an eluent. The desired product, mp 152 °C, was obtained as colorless crystals in 3.63 g (88%) yield. Found: C, 82.57; H, 5.79; N, 5.47%. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36 %. ^1H NMR ($CDCl_3$, δ): 1.15 (6H, s), 4.27 (1H, s), 7.3—7.7 (6H, m), 8.1— 8.4 (2H, m). IR (KBr): 2235, 1675, 710 cm^{-1}.

9-(1-Methoxycarbonyl-1-methylethyl)anthrone (**3**, *Z=COOCH*$_3$), mp 89—90 °C, was similarly obtained in 62% yield from anthrone and dimethyl azobisisobutyrate. Found: C, 77.53; H, 6.16%. Calcd for $C_{19}H_{18}O_3$: C, 77.49; H, 6.14%. ^1H NMR ($CDCl_3$, δ): 0.89 (6H, s), 3.61 (3H, s), 4.52 (1H, s), 7.3—7.6 (6H, m), 8.0—8.3 (2H, m). IR (KBr): 1730, 1670, 1317, 705 cm^{-1}.

9-(1-Cyano-1-methylethyl)anthracene (**5**, *Z=CN*). A solution of 0.807 g (3.1 mmol) of **3** (Z=CN) in 15 ml of ethanol was refluxed for 2 h, while a solution of 0.9 g (24 mmol) of sodium borohydride in 10 ml of 90% ethanol was added in 10 min. Water was added and the mixture extracted with dichloromethane. After evaporation of the solvent, **4** (Z=CN) was obtained in 0.77 g yield as a roughly equimolar mixture of *cis* and *trans* isomers. The alcohol (**4**, Z=CN) in 20 ml of carbon tetrachloride was heated under reflux for 1 h with 5 g of phosphorus pentaoxide and the mixture was filtered. The solvent was evaporated from the filtrate and the residue was chromatographed on alumina. A small amount (*ca.* 4%) of anthracene was eluted first and then came 0.46 g (61%) of **5** (Z=CN), mp 138 °C (recrystallized from ethanol). Found: C, 87.83; H, 6.18; N, 5.69%. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71%. ^1H NMR ($CDCl_3$, δ): 2.37 (6H, s), 7.3—7.6 (4H, m), 7.8—8.1 (2H, m), 8.40 (1H, s), 8.4—8.7 (2H, m). IR (KBr): 2230, 735 cm^{-1}.

9-(1-Methoxycarbonyl-1-methylethyl)anthracene (**5**, *Z=COOCH*$_3$), mp 123—125 °C, was similarly prepared in 41% yield. Found: C, 81.74; H, 6.46%. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52%. ^1H NMR ($CDCl_3$, δ): 2.12 (6H, s), 3.46 (3H, s), 7.2—7.6 (4H, m), 7.8—8.3 (4H, m), 8.37 (1H, s). IR (KBr): 1715, 1258, 1143, 717 cm^{-1}.

9-(1-Carbamoyl-1-methylethyl)anthracene. A solution of 1.0 g of **5** (Z=CN) and 5.0 g of potassium hydroxide in 50 ml of 2-ethoxyethanol was heated under reflux for 3 h under a nitrogen atmosphere. The mixture was treated with dilute hydrochloric acid after cooling and the precipitate was taken up in benzene. Evaporation of the solvent and recrystallization of the residue from tetrahydrofuran–hexane gave the amide, mp 226—227 °C. Found: C, 82.11; H, 6.45; N, 5.38%. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%. ^1H NMR ($CDCl_3$, δ): 2.13 (6H, s), 5.0 (2H, broad), 7.2—7.6 (4H, m), 7.7—8.1 (2H, m), 8.35 (1H, s), 8.1—8.5 (2H, m). IR (KBr): 3450, 3300, 3170, 1640, 735 cm^{-1}.

9-(1-Cyano-1-methylethyl)triptycene (**6**: *X=Y=H, Z=CN*). A solution of 2.00 g (8.16 mmol) of **5** (Z=CN) and 1.6 ml of isopentyl nitrite in 60 ml of dichloromethane was refluxed under a nitrogen atmosphere, while 1.45 g (10.6 mmol) of anthranilic acid in 40 ml of acetone was added in 50 min. The mixture was refluxed for further 30 min and the solvent was evaporated. The residue (2.40 g or 92% yield) was recrystallized to afford the desired material, mp 308—310 °C. Found: C, 89.42; H, 5.66; N, 4.26%. Calcd for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36%. ^1H NMR ($CDCl_3$, δ): 2.42 (6H, s), 5.30 (1H, s), 6.9—7.7 (10H, m), 7.8—8.0 (2H, m). IR (KBr): 2225 cm^{-1}.

9-(1-Methoxycarbonyl-1-methylethyl)triptycene (**6**: *X=Y=H, Z=COOCH*$_3$), mp 230—232 °C, was prepared similarly in 86% yield. Found: C, 84.75; H, 6.14%. Calcd for $C_{25}O_{22}O_2$: C, 84.71; H, 6.26%. ^1H NMR ($CDCl_3$, δ): 2.31 (6H, s), 3.75 (3H, s), 5.26 (1H, s), 6.8—7.5 (11H, m), 7.6—7.8 (1H, m). IR (KBr): 1740, 1715 cm^{-1}.

9-(1-Cyano-1-methylethyl)-1,2,3,4-tetrachlorotriptycene (**6**: *X=Y=Cl, Z=CN*). Similar treatment of 1.00 g of **5** (Z=CN) with tetrachloroanthranilic acid[7] afforded a mixture of products. The mixture was oxidized overnight with 1.75 ml of 30% hydrogen peroxide in 30 ml of formic acid at room temperature and diluted with water. The mixture was extracted with dichloromethane and the excess of peroxide was decomposed with iron(II) sulfate. Evaporation of the solvent followed by chromatography on alumina afforded the *dl* and the *meso* isomers of the desired compound in 0.407 g or 22% yield. The ratio *dl*/*meso* was *ca.* 11. The *dl* isomer was eluted first and was purified by recrystallization. The pure *meso* isomer was not obtained even though careful chromatographies were carried out.

The *dl* form, mp 289—291 °C. Found: C, 62.94; H, 3.02; N, 3.12; Cl, 30.72%. Calcd for $C_{24}H_{15}NCl_4$: C, 62.78; H, 3.29; N, 3.05; Cl, 30.88%. ^1H NMR ($CDCl_3$, δ): 2.43 (3H, s), 2.58 (3H, s), 6.08 (1H, s), 7.0—7.9 (7H, m), 8.3—8.5 (1H, m). IR (KBr): 2230 cm^{-1}.

The *meso* form exhibited the following signals in ^1H NMR spectrum, when those due to the *dl* form were subtracted from a spectrum of a *dl*-*meso* mixture ($CDCl_3$, δ): 2.71 (6H, s), 6.08 (1H, s), 7.0—7.6 (6H, m), 7.9—8.1 (2H, m).

9-(1-Methoxycarbonyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene (**6**: *X=Y=Cl, Z=COOCH*$_3$) was similarly prepared in 24% yield in total. The ratio *dl*/*meso* was 3.4.

The *dl* form, mp 286—288 °C. Found: C, 61.17; H, 3.74; Cl, 29.14%. Calcd for $C_{25}H_{18}O_2Cl_4$: C, 61.00; H, 3.69; Cl, 28.81%. ^1H NMR ($CDCl_3$, δ): 2.27 (3H, s), 2.48 (3H, s), 3.5—4.0 (3H, broad), 6.09 (1H, s), 6.9—7.6 (7H, m), 7.7—8.0 (1H, m). IR (KBr): 1740, 1720 cm^{-1}.

The *meso* form, mp 200—202 °C, solidified again on heating above the melting point and melted at the melting point of the *dl* form. High resolution MS: Found, M^+ 490.0001; Calcd for $C_{25}H_{18}O_2Cl_4$, 489.9943. ^1H NMR ($CDCl_3$, δ): 2.47 (6H, s), 3.70 (3H, s), 6.09 (1H, s), 6.9—7.6 (8H, m). IR (KBr): 1740, 1715 cm^{-1}.

9-(1-Cyano-1-methylethyl)-1,4-dimethyltriptycene (**6**: *X=CH*$_3$, *Y=H, Z=CN*) was similarly prepared from **5** (Z=CN) and 3,6-dimethylanthranilic acid[8,9] in 68% yield. The formation of the *meso* form was not detected by ^1H NMR spectra. Recrystallization of the product from tetrahydrofuran–hexane afforded pure *dl* form, mp 244—246 °C. Found: C, 89.66; H, 6.64; N, 4.04%. Calcd for $C_{26}H_{23}N$: C, 89.36; H, 6.63; N, 4.01%. ^1H NMR ($CDCl_3$, δ): 2.45 (3H, s), 2.47 (3H, s), 2.51 (3H, s), 2.89 (3H, s), 5.61 (1H, s), 6.75 (2H, s), 6.9—7.7 (7H, m), 8.1—8.3 (1H, m). IR (KBr): 2225 cm^{-1}.

The *meso* form was obtained in the following way. The *dl* form (0.717 g) was dissolved in 50 ml of *o*-dichlorobenzene and the solution was refluxed overnight. The solvent was evaporated and the residue was chromatographed on alumina to afford 0.047 g (7%) of the *meso* form. Recrystallization from tetrahydrofuran–hexane gave a pure material, mp 256—257 °C. High resolution MS: Found, M$^+$ 349.1802; Calcd for $C_{26}H_{23}N$, 349.1776. ^{1}H NMR ($CDCl_3$, δ): 2.55 (3H, s), 2.61 (3H, s), 2.62 (6H, s), 5.64 (1H, s), 6.82 (2H, s), 6.9—7.5 (6H, m), 7.8—8.1 (2H, m). IR (KBr): 2220 cm^{-1}.

9-(1-Methoxycarbonyl-1-methylethyl)-1,4-dimethyltriptycene (**6**: *X*=*CH*$_3$. *Y*=*H*, *Z*=*COOCH*$_3$) was similarly prepared. For the purification, the oxidation with performic acid was applied. A mixture of *dl* and *meso* forms was obtained in 60% yield. The ratio *dl*/*meso* was 11.

The *dl* form, mp 264—265 °C. Found: C, 84.74; H, 6.84%. Calcd for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85%. ^{1}H NMR ($CDCl_3$, δ): 2.29 (6H, s), 2.43 (3H, s), 2.52 (3H, s), 3.73 (3H, s), 5.62 (1H, s), 6.73 (2H, s), 6.8—7.5 (7H, m), 7.7—7.9 (1H, m). The signal at the highest field split into two in 1-chloronaphthalene at 70 °C. IR (KBr): 1740, 1710 cm^{-1}.

The *meso* form, mp 203—204 °C, was obtained by thin layer chromatography of a mixture which was rich in the *meso* form. The *meso* form resolidified at temperatures above the melting point and melted at the melting point of the *dl* form. High resolution MS: Found, M$^+$ 382.1853; Calcd for $C_{27}H_{26}O_2$, 382.1775. ^{1}H NMR ($CDCl_3$, δ): 2.40 (6H, s), 2.52 (3H, s), 2.65 (3H, s), 3.71 (3H, s), 5.61 (1H, s), 6.76 (2H, s), 6.8—7.5 (8H, m). IR (KBr): 1740, 1715 cm^{-1}.

Measurement of Spectra. ^{1}H NMR spectra were obtained with a Hitachi R-20B spectrometer, operating at 60 MHz. The temperature was 34 °C. IR spectra were obtained with a Hitachi EPI-G2 grating spectrophotometer and the wave numbers were calibrated with a polystyrene film. High resolution MS were obtained with a Hitachi RMH-1 spectrometer.

Measurement of Barriers to Rotation and Equilibrium Constants. Isomerization of the stable rotamers were carried out by heating solutions of the rotamers in 1-chloronaphthalene by immersing the samples in appropriate baths. The temperature of the baths was controlled by using the boiling points of solvents. The solvents were dimethyl sulfoxide (189 °C), *o*-dichlorobenzene (179 °C), mesitylene (162 °C), and cumene (152 °C). Analyses of the isomers were performed by either ^{1}H NMR spectroscopy or high pressure liquid chromatography using benzophenone as an internal standard. The chromatography apparatus was a Waters M-6000A equipped with a UV detector. The rate constants were obtained as usual.[10] Some of the rate constants were obtained by using the rate constants of the forward reaction and the equilibrium constant from the relation $k_{-1}=k/K$. The kinetic parameters were obtained by both the Arrhenius plot and the Eyring plot and the thermodynamic parameters by the common practice.

TABLE 1. EQUILIBRIUM CONSTANTS (K=*dl*/*meso*) OF **6** AT VARIOUS TEMPERATURES IN 1-CHLORONAPHTHALENE

Substituents			Temp/°C			
Z	X	Y	189	179	162	152
CN	Cl	Cl	7.5	8.4	8.8	9.6
CN	CH_3	H	15	16	16	17
$COOCH_3$	Cl	Cl	21	26	29	28
$COOCH_3$	CH_3	H	8.4	14	16	14

TABLE 2. THERMODYNAMIC PARAMETERS FOR EQUILIBRIA (*meso* ⇌ *dl*) OF ROTAMERS OF **6**

Z	X	Y	ΔH/kcal mol^{-1}	ΔS/eu
CN	Cl	Cl	−2.3	−1.0
CN	CH_3	H	−1.1	3.1
$COOCH_3$	Cl	Cl	−2.9	0.1
$COOCH_3$	CH_3	H	−4.9	−6.0

Results and Discussion

Conformational Equilibria. The equilibrium constants of the rotamers at various temperatures are given in Table 1 and the thermodynamic parameters obtained from these results in Table 2. Clearly all the *dl* isomers are strongly favored over the *meso*. Since it is known that compounds, which do not have a substituent in the peri position, give values very close to 2 which is a statistical factor,[11,12] the equilibrium constants in Table 1 are unusual. The unusuality must be caused by the presence of the peri-substituent which is close to the substituent in the 9-position. The preference of the *dl* form must be attributed to the steric repulsion between the substituents in 1 and 9 positions, because methyl is a larger group than the sp^2 or sp moieties.[13]

Close examination of the data in Table 1 discloses, however, an interesting point. Namely, the chloro group favors the *dl* form to a sizable extent relative to the methyl group in the methoxycarbonyl compounds. The tendency is reversed in the cyano compounds, however. Since the chloro group is smaller than the methyl in its size, the consideration of repulsive interactions predicts that the methyl group should disfavor the *meso* form relative to the chloro group. This is the case of the cyano compounds but, in the methoxycarbonyl compounds, the methyl group favors the *meso* form. The anomaly in the population ratio of the compound **6** (X=Y=Cl, Z=$COOCH_3$) may be at least partly attributed to atrractive interactions between the chloro group and the methoxycarbonyl group[14] which favor the *dl* form.

Barriers to Rotation. Rate constants of isomerization of the rotamers at 189 °C are summarized in Table 3 and activation parameters obtained from the rate constants at the 4 temperatures are shown in Table 4. Arrhenius parameters are added to facilitate the comparison of the data with those of **2**.

It is interesting to note that barriers to rotation of the compounds examined here are all lower than that of compound **2**. It is especially so in the case of the pro-

TABLE 3. RATE CONSTANTS FOR ISOMERIZATION OF ROTAMERS OF **6** AT 189 °C

Z	X	Y	k/s^{-1}	
			(*dl*→*meso*)	(*meso*→*dl*)
CN	Cl	Cl	6.30×10^{-5}	4.71×10^{-4}
CN	CH_3	H	4.94×10^{-5}	7.24×10^{-4}
$COOCH_3$	Cl	Cl	2.40×10^{-4}	4.94×10^{-4}
$COOCH_3$	CH_3	H	3.81×10^{-4}	3.19×10^{-4}

TABLE 4. ACTIVATION PARAMETERS FOR INTERNAL ROTATION OF **6** AND **2**

Z	X	Y	Process	E_a kcal/mol	log A	$\Delta H^{\ne}$ kcal/mol	$\Delta S^{\ne}$ eu
CN	Cl	Cl	*dl*→*meso*	36.1	12.9	35.3	−2.3
			meso→*dl*	33.8	12.7	32.9	−3.3
CN	CH_3	H	*dl*→*meso*	36.7	13.1	35.8	−1.6
			meso→*dl*	35.4	13.6	34.6	1.0
$COOCH_3$	Cl	Cl	*dl*→*meso*	34.4	12.6	33.5	−3.6
			meso→*dl*	31.2	12.4	30.3	−4.4
$COOCH_3$	CH_3	H	*dl*→*meso*	29.1	10.2	28.2	−14.5
			meso→*dl*	24.3	9.0	23.4	−20.3
Compound **2**[4]				37.7	13		

cesses *meso*→*dl*. It is tempting to consider that the interaction between the peri-substituent and the methyl group in the 9-substituent is much larger than that involving the cyano or the methoxycarbonyl group. Thus the ground state is raised relative to the transition state for rotation to lower the barrier. The tendency is reverse with the case of 9-isopropyltriptycenes,[15] where the introduction of a larger substituent in the peri-position led to the increase in the barrier height. 9-Benzyltriptycenes exhibited higher barriers to rotation by introducing substituents in two peri positions.[16] The congestedness of the molecule in the ground state is evident from the molecular models and the fact that the rotational isomers are isolated. X-Ray analysis of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene supports the idea: the molecule has unusual bond lengths and bond angles.[17] Therefore, relief of the steric strain to a small extent will lower the energy level of the ground state to a fair extent. This is reflected in the equilibrium constants discussed above. The higher barriers of the nitriles relative to the esters may be attributed to the lowering of the ground state also. A report by Anderson *et al.*[18] gives the similar explanation for the fact that the cyano group exhibited the highest barrier to rotation among compounds $(CH_3)_3C\text{–}C(CH_3)_2X$ where X was CN, CHO, CO_2H, CH_3CO, or $C(CH_3)\text{=}CH_2$.

Compound **6** (X=Y=Cl, Z=$COOCH_3$) was expected to show a higher barrier than others because the ground state is stabilized due to the attractive interaction between the chloro and the methoxycarbonyl groups. However, the barriers are by and large the same. Although the phenomenon must partly be attributed to the raise in the ground state due to steric reasons, other possibilities like solvation effects may not be ruled out. One notes that the frequency factors (and entropies of activation) and activation energies of compound **6** (X=CH_3, Y=H, Z=$COOCH_3$) are unusually small. The reasons for this phenomenon are not well understood at the present time.

It now seems to be necessary to remove the peri-substituents in order to raise the barriers to rotation of 9-(1-cyano or 1-methoxycarbonyl-1-methylethyl)triptycenes. A work along this line is in progress.

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