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Restricted Rotation Involving the Tetrahedral Carbon. I. Some Diels-Alder Adducts Derived from 9-Substituted Anthracenes

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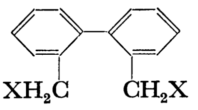
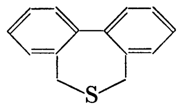
9-*t*-Butylanthracene was treated with dimethyl acetylenedicarboxylate and benzoquinone to give Diels-Alder adducts. The NMR spectra of these adducts suggest that the internal rotation about the C_1–C_{Bu} bond is not taking place on the NMR time scale. On the other hand, a Diels-Alder adduct prepared from 9-isopropylanthracene and dimethyl acetylenedicarboxylate shows the coalescence phenomenon of the NMR signals when the temperature is raised. The possibility of optical resolution due to hindered rotation about the sp^3–sp^3 carbon bond is pointed out.

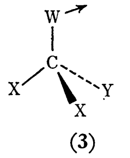
There have been numerous examples of restricted rotations about the carbon-carbon single bonds. However, since the confirmation of the restricted rotation depends on the optical resolution, the identified examples have been limited to fairly stable isomers; in other words, a highly restricted rotation was necessary in order to note the hindered rotation. Optical resolutions of numerous biphenyl derivatives$^{1)}$ and ansanoid compounds$^{2)}$ are examples of this.

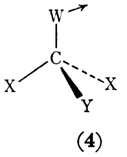
In recent years, it has become possible to study the internal rotation by means of NMR spectroscopy. This method has enabled us to study the exchange of protons as fast as 10^0—10^3 sec^{-1}. Prior resolution is not now necessary to study fairly fast internal rotation. Biphenyls$^{3)}$, ketones$^{4)}$ and ansanoids$^{5)}$ have thus been studied by virtue of either the presence of dissymmetric protons of methylene, isopropyl, or other groups (*e.g.* **1**) or the different chemical shifts in the ring system (*e.g.* **2**).

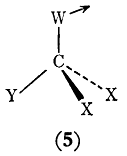

(**1**)


(**2**)

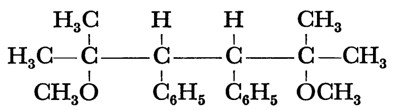
In the biphenyls and ketones, the pivot bond in question is the C_{sp^2}–C_{sp^2}, whereas in ansanoids the pivot bond is C_{sp^2}–C_{sp^3}. A very important point should be raised here. That is, in the tetrahedron theory of carbon, it is assumed that the rotation about the C–C single bond is free; otherwise, even a compound which has no asymmetric carbon could be resolved into optical isomers. Let us consider a molecule, C_{WXXY}, in which W is not spherically symmetric and is directed.$^{6)}$ We can then write three stable conformations for the molecule, **3**, **4**, and **5**, where the arrow attached to W represents the direction of W. If the rotation about the W–C bond is free in the sense of classical organic chemistry, the molecule will not have any isomer, as the tetrahedron theory predicts. However, if the rotation about the W–C bond is slow, there will be three isomers for the C_{WXXY} molecule. The mirror image of **5** is identical with **5**, whereas **3** and **4** are mirror images of each other and are not identical. It will be proper to call **5** the *meso*-form, and **3** and **4** *dl*-form.


(3)


(4)


(5)

Since W can involve either sp^2- or sp^3-hybridized carbon in connecting with the C_{XXY} group, the restricted rotation in either the sp^2–sp^3 or the sp^3–sp^3 C–C bond could cause the isolation of the afore-mentioned isomers. There have been several papers concerning the above phenomena, but not much notice has been taken of the importance of the phenomenon.$^{7)}$ As early as 1961, Brownstein$^{8)}$ reported the NMR results of *meso*- and *dl*-forms of 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (**6**) and pointed out the possibility of the presence of rotational isomers from the appearance of two sets of signals. However,



$$\begin{array}{ccccccc} & H_3C & & H & & H & & CH_3 & \\ H_3C- & C & — & C & — & C & — & C & -CH_3 \\ & CH_3O & & C_6H_5 & & C_6H_5 & & OCH_3 & \end{array} \quad (6)$$

the close examination of the spectra of the pairs led the present authors to doubt the presence of the conformers. Rather, the spectra can best be interpreted by assuming the contamination by the other isomers, the *meso*- and *dl*-forms. Therefore, in our opinion, these data are not conclusive in establishing the restricted rotation about the central C_{sp^3}–C_{sp^3} bond.

There are, of course, many cyclic compounds, the

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1) R. Adams and H. C. Yan, *Chem. Rev.*, **12**, 261 (1932).

2) A. Luttringhaus and G. Eyring, *Ann.*, **604**, 111 (1957); A. T. Blomquist, R. E. Stahl, and Y. C. Meinwald, *J. Org. Chem.*, **26**, 1687 (1961).

3) M. Ōki, H. Iwamura, and N. Hayakawa, This Bulletin, **36**, 1542 (1963); *ibid.*, **37**, 1855 (1964); R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964); W. L. Meyer and R. B. Meyer, *J. Amer. Chem. Soc.*, **85**, 2170 (1963).

4) M. Ōki and N. Nakamura, unpublished work.

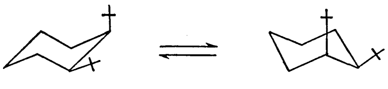
5) M. Nakazaki, K. Yamamoto, and S. Okamoto, *Tetrahedron Lett.*, **1969**, 4597.

6) M. Ōki, "Rittaikagaku (Stereochemistry)" Tokyo Kagaku Dojin, Tokyo (1961), p. 5.

7) a) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, **1967**, 27; J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, *J. Chem. Soc., C.* **1968**, 664; G. P. Newsoroff and S. Sternhell, *Tetrahedron Lett.*, **1967**, 2539; c) E. A. Chandross and C. F. Sheley, Jr., *J. Amer. Chem. Soc.*, **90**, 4345 (1968); d) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969); e) A. Riecker and H. Kessler, *Tetrahedron Lett.*, **1969**, 1227.

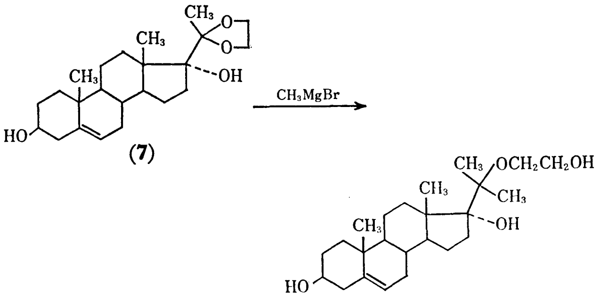
8) S. Brownstein, *Can. J. Chem.*, **39**, 1677 (1961).

conformations of which are frozen at the lower temperature, and even the equatorial isomer of chlorocyclohexane[9] has been isolated. However, these isomers are unstable at room temperature. *cis*-1,2-Di-*t*-butylcyclohexane has been reported by Kessler *et al.*[10] to have nonequivalent *t*-butyl groups in its NMR spectrum at room temperatur , and the two signals coalesce at 35°C. These results indicated that two *t*-butyl groups on the cyclohexane ring are not good enough to isolate the rotational isomers about the C_{sp^3}–C_{sp^3} bond, although the cyclohexane ring and the bulkiness of the *t*-butyl groups are considered to be favorable for freezing the conformations.



(or twisted boat conformations)

Recently Scheer *et al.* isolated a pair of isomers on treating the ethylene ketal (**7**) with methylmagnesium bromide.[11]



(**7**)

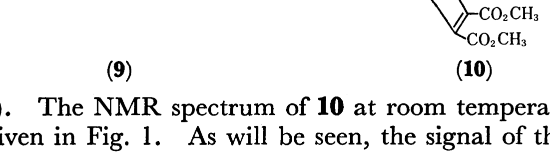
(**8**)

They claim that these isomers (**8**) result from the restricted rotation about the C_{17}–C_{20} bond. The present authors have a feeling that this example is too complicated to demonstrate the presence of the isomers clearly and that simpler examples are needed.

We wish to report our findings about the restricted rotation in the Diels-Alder adducts of 9-substituted anthracene and point out the possibility of isolating the rotational isomers.

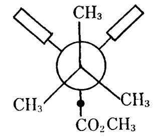
Results and Discussion

The treatment of 9-*t*-butylanthracene (**9**) with dimethyl acetylenedicarboxylate gave dimethyl 1-*t*-butyldibenzo[*b*,*e*]bicyclo[2.2.2]octatriene-7,8-dicarboxylate



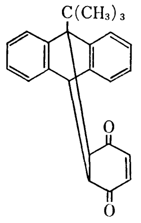
(**9**) (**10**)

(**10**). The NMR spectrum of **10** at room temperature is given in Fig. 1. As will be seen, the signal of the *t*-butyl group is split into two, the relative area being 1:2. This result can best be interpreted by assuming the restricted rotation about the C_1-C_{Bu} bond. Namely, the Newman projection (**11**) through the C_1-C_{Bu}

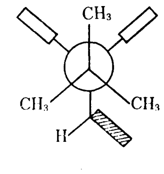


(**11**)

bond clearly explains why the *t*-butyl group should show two signals at the different chemical shift: the two methyls are equivalent, but the last methyl is located in a magnetically non-equivalent environment. Additional support for the above assignment can be obtained by looking at the NMR spectrum of 1-*t*-butyl-9,10:11,12-dibenzotricyclo[6.2.2.$0^{2,7}$]dodeca-4,9,11-triene-3,6-dione (**12**), which was prepared from **9** and *p*-benzoquinone. The Newman projection (**13**) of this compound shows that no pair of the three methyl groups are equivalent to each other; indeed, the NMR spectrum (Fig. 2) shows three methyl signals.



(**12**)



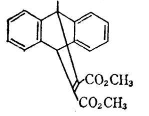
(**13**)
The shaded rectangle indicates the cyclohexenedione ring.

The two methyl signals of **10** are found not to coalesce even at 132°C. Thus, using the chemical-shift difference ($\Delta\nu_0$) and putting 405°K into Eq. (1), the free energy ($\Delta G^{\neq}$) of the activation for rotation is estimated to be not lower than 25 kcal/mol.

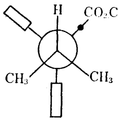
$$\Delta G^{\neq} = -RT\ln\frac{\pi h(\Delta\nu_0)}{\sqrt{2}\,kT} \tag{1}$$

It will be possible to isolate isomers of this kind, since, if the free energy of activation is 20—30 kcal/mol, the isolation of isomers is possible at room temperature in biphenyl derivatives. Study along these lines is now in progress.

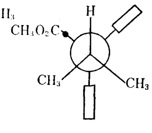
In an attempt at isolating the *meso*- and *dl*-forms of **3**—**5** type, the *t*-butyl group is now switched to the isopropyl goup: W, X, and Y are 2,3-dimethoxycarbonyl-5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-trien-1-yl, methyl, and hydrogen respectively. The isopropyl derivative (**14**) was prepared analogously with the other compounds.



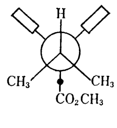
(**14**)



(**15**)



(**16**)



(**17**)

The NMR spectrum (Fig. 3) of **14** at room temperature shows a pair of doublets for the methyl groups

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[9] F. R. Jensen and C. H. Bushweller, *J. Amer. Chem. Soc.*, **88**, 4279 (1966); *ibid.*, **91**, 3223 (1969).

[10] H. Kessler, V. Husowski, and M. Hanack, *Tetrahedron Lett.*, **1968**, 4665.

[11] F. Kohen, R. A. Mallory, and I. Scheer, *Chem. Commun.*, **1969**, 580.

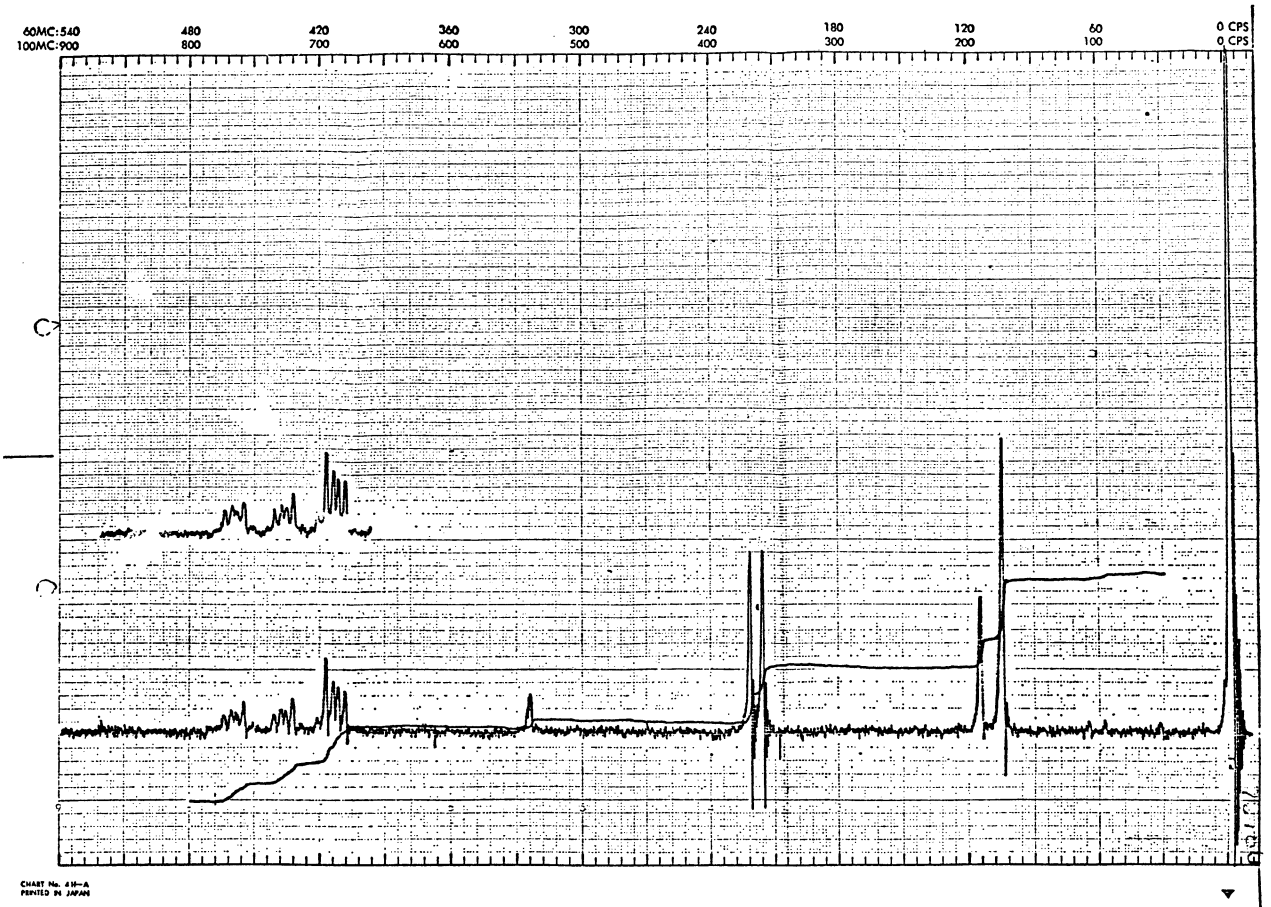

Fig. 1. NMR spectrum of dimethyl 1-*t*-butyldibenzo[*b*,*e*]bicyclo[2.2.2]octatriene-7,8-dicarboxylate at 60 MHz.

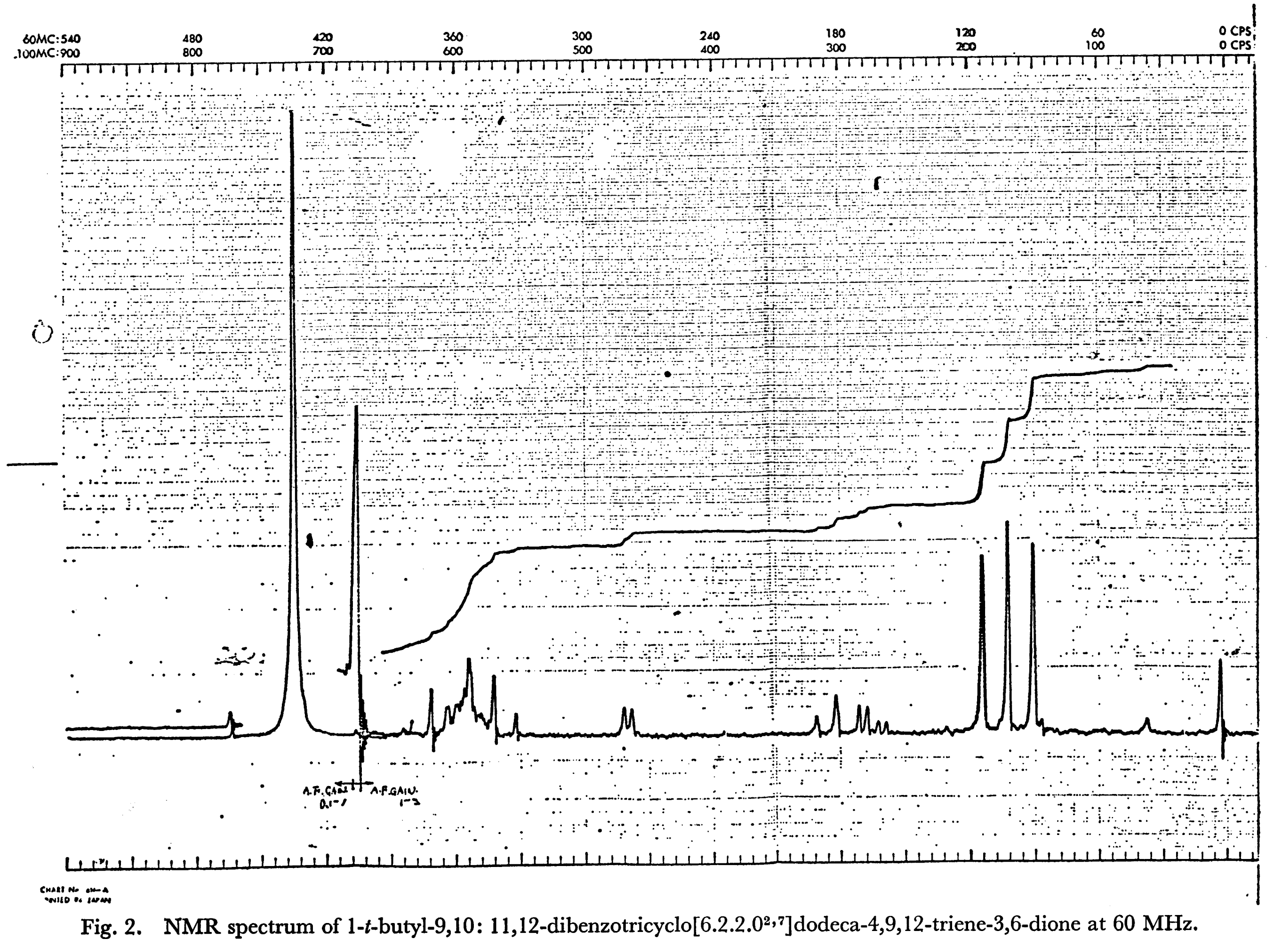

Fig. 2. NMR spectrum of 1-*t*-butyl-9,10: 11,12-dibenzotricyclo[6.2.2.0^{2,7}]dodeca-4,9,12-triene-3,6-dione at 60 MHz.

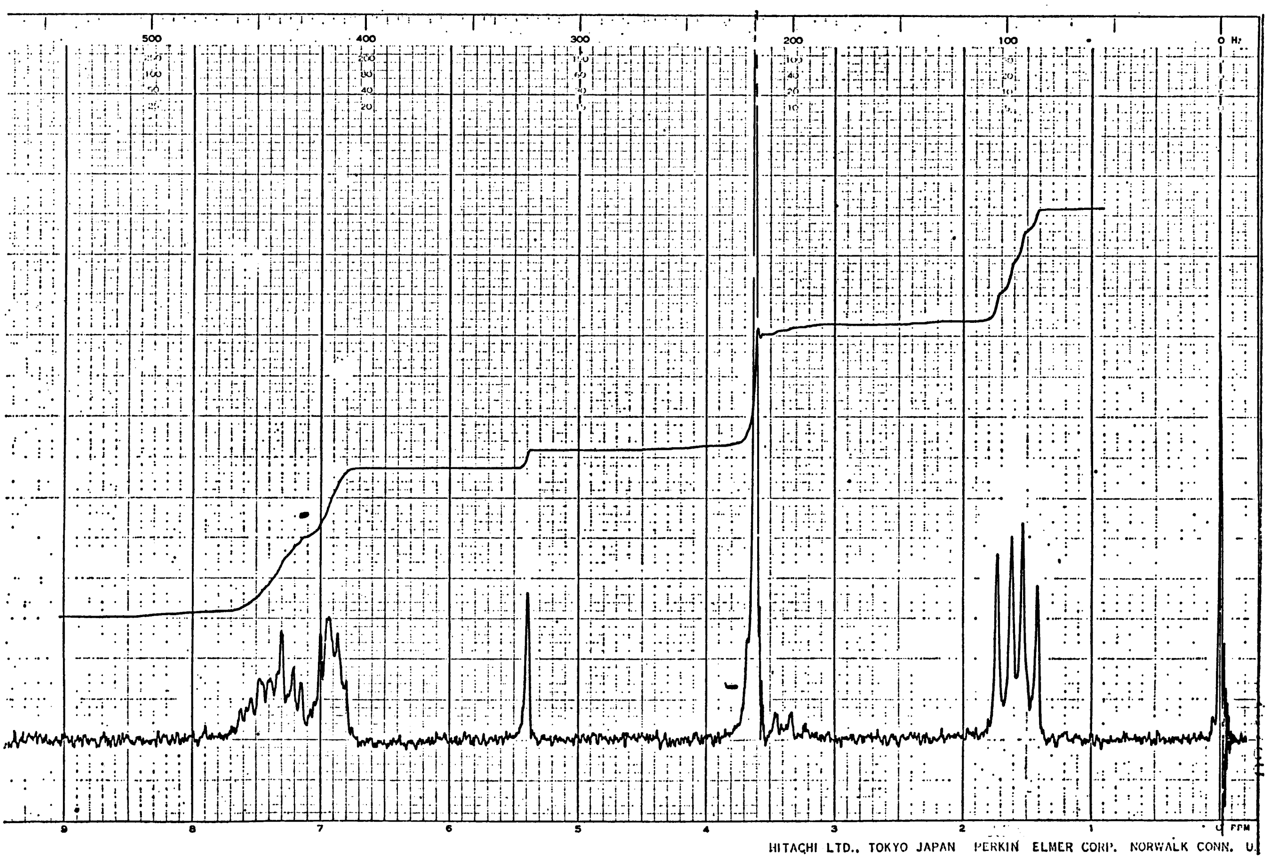

Fig. 3. NMR spectrum of dimethyl 1-isopropyldibenzo[*b,e*]bicyclo[2.2.2]octatriene-7,8-dicarboxylate at 60 MHz at room temperature.

in the isopropyl. The intensities are identical within the range of error. Since it may be assumed that methyl signals of the *meso*-form (**17**) are very close to one of the methyl groups in the *dl*-form (**15** and **16**), if the *meso*-form were present in a substantial amount, one of the methyl signals would have been stronger than the other. Thus, the absence of the other signals for the methyl groups of the isopropyl and the almost identical intensities of the pair of doublets indicate that the population of the *meso*-form will be very small, if present at all.

This can be interpreted by assuming that either the *meso*-form is thermodynamically less stable than the *dl*-form or the formation of the former is kinetically less favored than the latter. Either case is possible at the present stage, since the group carrying the methoxycarbonyl group is expected to be larger than the benzo group and the approach of the dimethyl acetylenedicarboxylate molecule from the side where two methyl groups are present will be disfavored relative to the side where a methyl and a hydrogen are present.

When the temperature is raised, the coalescence of the pair of doublets in the NMR spectra is observed. The T_c is 64°C in tetrachloroethane. The free energy of activation for the rotation about the C_{Pr}-C_1 bond is now obtained as 17.7 kcal/mol, using Eq. (1). From the temperature dependence of the half-band width of the signals the rate constants (k) can be obtained by Eq. (2):

$$k = \frac{\pi(\Delta\nu_0)^2}{2(W-W_0)} \qquad (2)$$

where W_0 is the half-band width with an infinitely fast exchange rate and W, the half-band width at the observed temperature. The Arrhenius plot of log k *vs.* $1/T$ afforded E_a of 15.4±1.0 kcal/mol.

On the other hand, the free energy of activation ($\Delta G_c^{\ddagger}$) at the coalescence temperature is obtained by Eqs. (3) and (4):

$$k_c = \frac{\pi}{2}\Delta\nu_0 \qquad (3)$$

$$\Delta G_c^{\ddagger} = -\boldsymbol{R}T\ln\frac{hk_c}{k_BT} \qquad (4)$$

where k_B is the Boltzmann constant.

It is, then, possible to derive $\Delta H_c^{\ddagger}$ and $\Delta S_c^{\ddagger}$ by putting these values into Eyring's equations, (5) and (6):

$$\Delta H_c^{\ddagger} = E_a - \boldsymbol{R}T \qquad (5)$$

$$\Delta S_c^{\ddagger} = \frac{1}{T}(\Delta H_c^{\ddagger} - \Delta G_c^{\ddagger}) \qquad (6)$$

$\Delta H_c^{\ddagger} = 14.4 \pm 1.0$ kcal/mol and $\Delta S_c^{\ddagger} = -10 \pm 1$ e. u. are thus obtained. These values suggest that, at 20°C, the rate constant is 0.78 sec^{-1} or the half-life time is 0.9 sec. Thus, in order to resolve this compound (**14**) into optically active isomers, the compound will have to be handled at the lower temperature.

The chemical shift of the methyl signal is 1.49 ppm from TMS at 130°C, whereas the average of the chemical shift of the methyl signals at room temperature is 1.55. This small change in the average chemical shifts may mean that the contribution of the conformation (**17**) is very little, even at 130°C. It could also be deduced that the internal rotation occurring in **14** is not the full rotation, but the movement to and fro, in which the transition state is the eclipsing of the hydrogen of the isopropyl group and the methoxycarbonyl group. This assumption readily explains why the internal rotation in the *t*-butyl compound (**10**) is so much restricted, while that in the isopropyl compound (**14**) occurs with fair ease, for the methoxycarbonyl group is bulkier than the benzo group, as judged from the isomer distribution of **14**.

Experimental

Spectral Measurement. The NMR spectra were recorded on either a JEOL C-60H or Hitachi R-20A spectrometer. The temperature reading was calibrated by measuring the chemical shift difference between methylene and hydroxyl protons of ethylene glycol.

*Dimethyl 1-*t*-Butyldibenzo*[b, e]*bicyclo[2.2.2]octatriene-7,8-dicarboxylate (10).* An equimolar mixture of 9-*t*-butylanthracene[12] and dimethyl acetylenedicarboxylate was heated slowly until all the solid fused; the heating was then continued for several more minutes. The recrystallization of the product from either methanol or ethanol gave the desired product; mp 182—183°C.

Found: C, 76.65; H, 6.65%. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%.

Dimethyl 1-Isopropyldibenzo [b, e] *bicyclo [2.2.2] octatriene-7, 8-dicarboxylate* (*14*) was similarly prepared; mp 143.5—144.5°C

Found: C, 75.95; H, 6.20%. Calcd for for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

*1-*t*-Butyl-9, 10, 11, 12-dibenzotricyclo* [6.2.2.$0^{2,7}$]*dodeca-4,9, 12-triene-3,6-dione* (*12*). 9-*t*-Butylanthracene (4 g) and 3 g of benzoquinone in xylene were heated under reflux. The crystals obtained on cooling were recrystallized from ethanol; mp 161—166° (dec.).

Found: C, 83.93; H, 6.73%. Calcd for $C_{24}H_{22}O_2$; C, 84.17; H, 6.47%.

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[12] R. C. Parish and L. M. Stock, *J. Org. Chem.*, **31**, 4265 (1966).