Hindered Rotation Around the C(9)–CH_2Cl Bonds in Chloromethyltriptycenes

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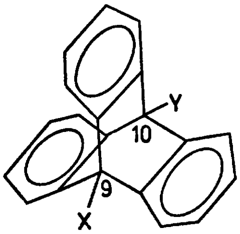
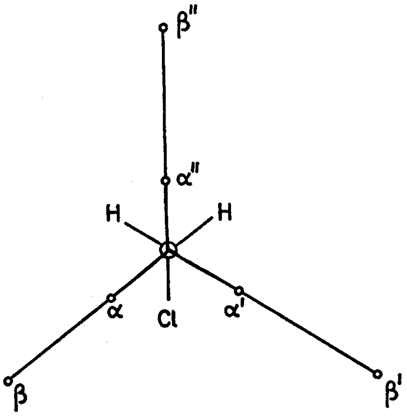
Summary A strikingly high (*ca.* 16 kcal/mol) barrier to rotation around the C(9)–CH_2Cl bond in chloromethyltriptycenes has been detected by temperature-dependent n.m.r. spectroscopy.

As a rule, barriers to rotation around normal carbon–carbon bonds in ethane-like molecules are below 5[1] but the barrier can be as high as 10 kcal/mol for sterically crowded bonds, and so could be studied by dynamic n.m.r. spectroscopy.[2,3] We now report an extremely high barrier to rotation around the C(9)–CH_2Cl bond, in a study of the n.m.r. spectra of triptycenes (I) and (II) substituted at the bridgehead. The n.m.r. spectra [60 MHz; tetrahydrofuran (THF) solvent; room temp.] of (I) and (IV) are shown in Figure 1a—d.



(I; X=CH_2Cl, Y=CH_2Cl)
(II; X=CH_2Cl, Y=H)
(III; X=H, Y=H)
(IV; X=Bz, Y=Bz)



(V)

In the spectrum of triptycene itself (Figure 1a) the assignment of the high-field aromatic band to the β-H has been proved.[4,5] The α-H signals are slightly broadened owing to weak spin–spin coupling between the α- and bridge protons. Compound (IV) gives a symmetrical AA'BB' spectrum (Figure 1b). Protons on different aromatic rings in (I)–(IV) are probably not subject to mutual spin–spin coupling, and it is also reasonable to assume that (IV) has the same symmetry as triptycene (III).

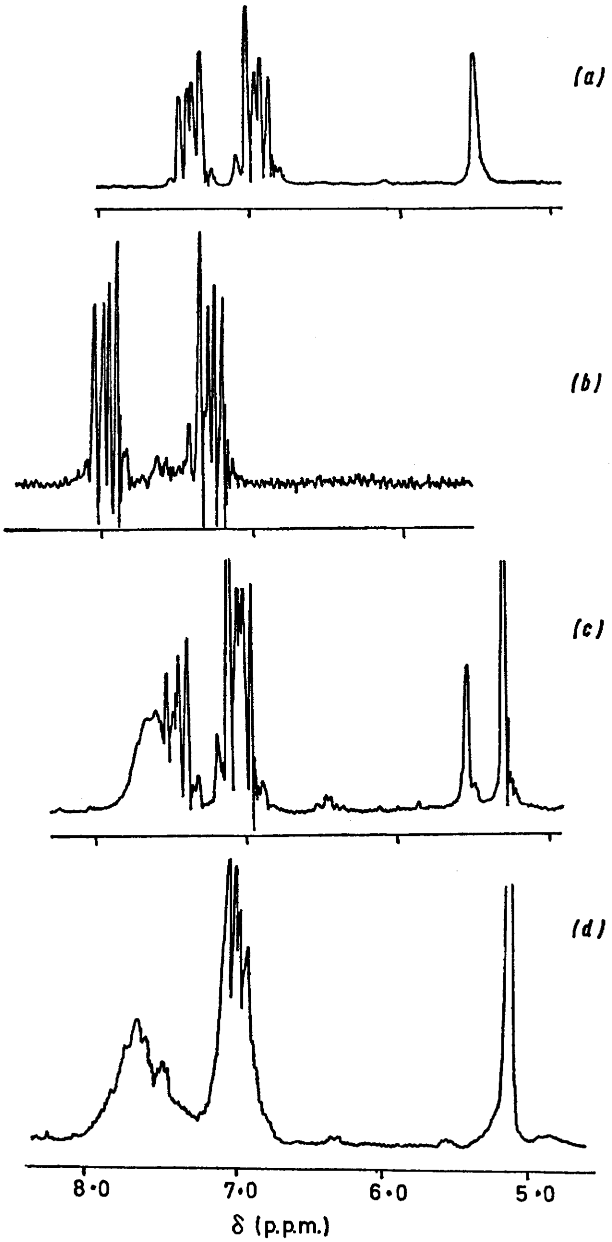


Figure 1. ^1H *N.m.r. spectra* (60 *MHz*) *of triptycene and its derivatives in THF at room temperature:* (*a*), *compound* (III); (*b*), *compound* (IV); (*c*), *compound* (II); (*d*), *compound* (I).

The significant broadening in the low-field band in the spectrum of (II) (Figure 1c), could be ascribed to the fact that the molecular symmetry is distorted; an ABCD type spectrum is observed for each aromatic ring (if A and B are both α-protons, $\delta_A - \delta_B > \delta_C - \delta_D$) instead of the AA'BB' type spectrum for (III) and (IV). For (I), however, as well as for (IV), the symmetry is higher, and so the spectrum should have become sharper. In reality, however, the broadening is even more pronounced and is observed at higher fields (in the aromatic region). Weak spin–spin coupling between the aromatic (especially α) protons and the $ClCH_2$ protons was ruled out by double resonance experiments.

We thought that the broadening was due to a dynamic process relative to the n.m.r. time scale and that it might be temperature-dependent. The spectrum of (I) becomes noticeably less diffuse even on moderate heating (50° in THF), and so was studied over a wider temperature interval, +20 to +100 °C, in hexamethylphosphoramide (Figure 2a—e). The spectrum clearly sharpens with temperature, the high-field region collapsing more rapidly. Above 90°, a symmetrical AA'BB' spectrum, typical of 9,10-disubstituted triptycenes [*e.g.* that for (IV) in Figure 1], is observed.

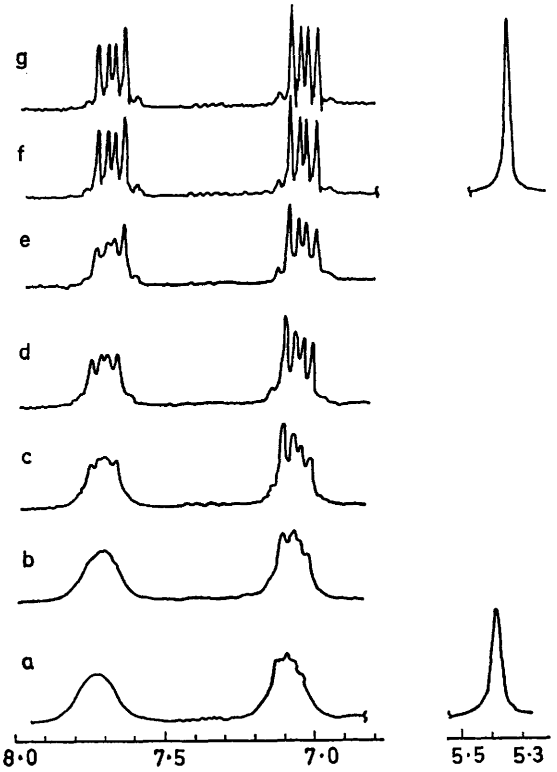


FIGURE 2. ^{1}H *N.m.r. spectrum* (100 *MHz*) *of* 9,10-*di*(*chloromethyl*)*triptycene in hexamethylphosphoramide at various temperatures* (°*C*): (*a*), +30; (*b*), +40; (*c*), +50; (*d*), +60; (*e*), +70; (*f*), +80; (*g*), +90.

We believe that at lower temperatures there exist rigid configurations (conformations) of (I) wherein the CH_2Cl groups are arranged differently with respect to the aromatic rings. This should lead to the different shielding of the α-protons ($\delta_\alpha = \delta_{\alpha'} \neq \delta_{\alpha''}$; Figure 1a) and, to a lesser extent, of the β-protons.

The second $CHCl_2$ group in (I) is hindered with respect to the C(9)–CH_2Cl bond, so that, even if the mutual orientation of the two chloromethyl groups is neglected, the non-equivalence of the protons will increase ($\delta_\alpha \neq \delta_{\alpha'} \neq \delta_{\alpha''}$).[†]

One might, thus, expect to observe at least two sets of signals for the α-protons in the lower limit of the exchange process. In the spectra of (I) (−30 °C; THF) (Figure 3) the α-protons give rise to two sets of signals: at 7·7 [4H, probably those nearest to Cl of the CH_2Cl groups for a rigid conformation (V); α- and α'-H], and 7·1 p.p.m. [2H; α''-H for conformation (V)]. The 7·1 p.p.m. signal is superimposed with the rather complex β-H signal at 7·0 p.p.m.

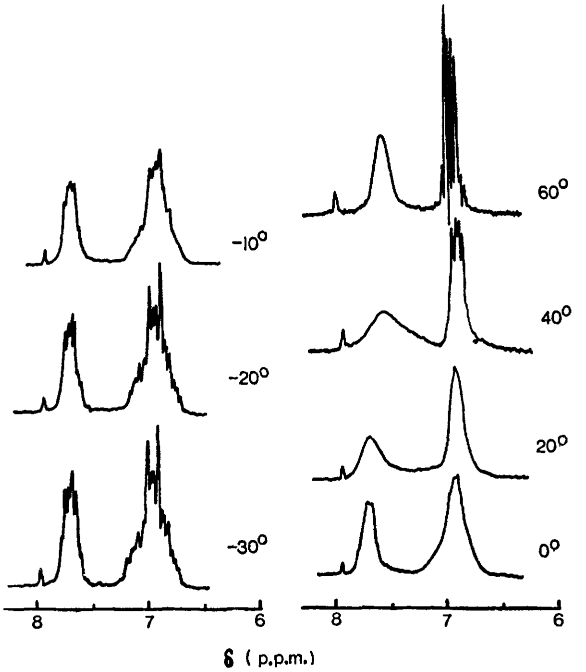


FIGURE 3. ^{1}H *N.m.r. spectra* (100 *MHz*) *of* 9,10-*di*(*chloromethyl*)-*triptycene in THF at various temperatures. The lowest-field signal is attributed to an impurity. This signal can be used for control of resolution.*

At 0—10 °C (Figure 3) the α-proton signals coalesce. Similar temperature-dependent spectra were also observed for (II) (solutions in THF and hexamethylphosphoramide).

Quantitative study of the rate constants, *k*, for the observed rotation is hindered by strong spin coupling for the systems under study. On the basis of the low-temperature spectra (Figure 3) we believe that the low-limit exchange takes place at −20 °C where a very slight broadening (but not collapse) of the multiplet structure is observed. This temperature can be assumed to be the temperature of stereochemical rigidity.[‡] Owing to the uncertainty in determining T_r (±5°) only an approximate estimate of the free energy of activation for the rotation can be made. For both (I) and (II) $\Delta G(250\ K) = 16 \pm 2$ kcal/mol. Such a high barrier to internal rotation may be caused by

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[†] The conformers which differ in the mutual orientation of the chloromethyl groups of (I) cause the broadening of the $CHCl_2$ signal, followed by the coalescence at higher temperatures (Figure 2).

[‡] T_r is defined as the temperature at which $k = 1\ s^{-1}$; in other words exchange broadening of *ca.* $1/\pi$ Hz (see also ref. 6) is observed.

spatial hindrance characteristic of triptycene and its derivatives.

Compounds (I)—(IV) were synthesised from anthracene or derivatives and benzyne generated from benzenediazonium *o*-carboxylate; satisfactory m.p.s were obtained.[7]

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