HETERA-p-CARBOPHANES.   II.   BULKINESS OF METHOXYL GROUP AS REVEALED

BY INTERNAL ROTATION OF DIHETERA[16]PARACYCLOPHANES.[1]

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Role of the methoxyl group in giving steric effects on the internal rotation
is well documented. Adams and his coworkers compared the rates of racemization
of 2'-substituted 5'-methyl-6-nitrobiphenyl-2-carboxylic acids and found that
methyl is the more effective group in giving the steric hindrance than the
methoxyl.[2] Likewise, the rates of racemization of 3'-substituted 2'-methoxy-6-
nitrobiphenyl-2-carboxylic acids suggest that the methoxyl group is less effective
in giving the buttressing effect than the methyl.[3] In one of the recent papers
from this laboratory, it was also noted that the methoxyl group gave less steric
hindrance than bromine, which has almost the same van der Waals radius with the
methyl group, in internal rotation of some aromatic ketones.[4]

From the stand point of the common sense, however, the above findings are
unusual because the methoxyl group contains more atoms than the methyl. It is
assumed that, by taking a conformation in which the methoxy methyl group is far
from the site of interaction, the oxygen only becomes the part giving the steric
hindrance. This assumption is partly supported by the fact that 2-alkylbiphenyls
give UV absorption maxima at almost the same wave lengths with almost the same
extinction coefficients irrespective to the chain length of the straight-chain
alkyl group.[5] The above discussion implies that, if there is an example of
compounds which exhibit the steric hindrance of the methoxyl group as a whole,
the methoxyl group should be bulkier than the methyl group, contrary to the earli-
er findings. We now wish to report our finding of such an example.

Diaza- and dioxa-[16]paracyclophanes which carry two methoxyl groups at the

benzene ring were synthesized and the barriers to rotation compared with those of compounds which carry methyl groups instead of the methoxyl. The methods of syntheses of these compounds were essentially the same as reported previously: 2,5-dimethoxy-1,4-phenylenediacetyl dichloride (1) was treated with 1,10-decane-diamine or 1,10-decanediol under the high dilution conditions. 3,14-Diaza-18,21-dimethoxy-2,15-dioxo[16]paracyclophane (2b), mp 198.0-199.5°C, and 3,14-dioxa-18,21-dimethoxy-2,15-dioxo[16]paracyclophane (3b), mp 63.0-64.0°C, thus obtained gave satisfactory analytical and mass-spectral data. The synthesis of 3,14-diaza-18,21-dimethyl-2,15-dioxo[16]paracyclophane (2a) was reported earlier and 3,14-dioxa-18,21-dimethyl-2,15-dioxo[16]paracyclophane (3a), mp 89.0-90.0°C, was prepared similarly.

The ^{1}HNMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. The chemical shifts were determined from the internal $Cl_2CHCHCl_2$ and converted to the usual δ values from TMS.
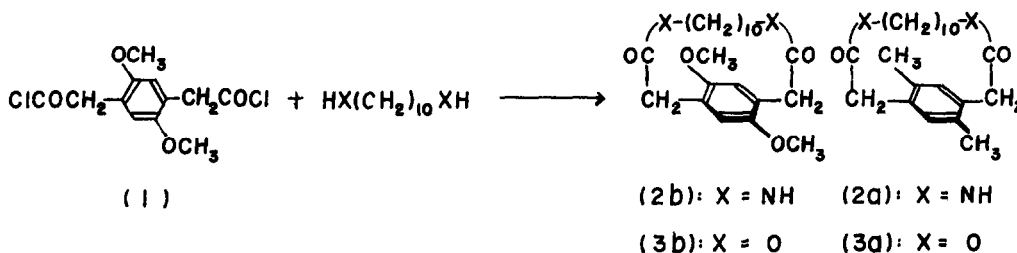
The ^{1}HNMR spectrum of 2a in $CDCl_3$ at 34°C showed a singlet for the benzylic protons, whereas that of 2b under the same conditions possessed an AB-type quartet. This must be taken as an indication that, as reported previously,[1] the rotation of the aromatic ring in 2b is slow on the NMR time scale, whereas that

Table 1. ^{1}HNMR (60 MHz) and kinetic data for
rotation of the aromatic rings

compound	$\Delta\delta_{AB}$ (Hz)	J_{AB} (Hz)	Tc (°C)	$\Delta G_c^{\ddagger}$ (kcal/mole)	solvent
2a[1]	(14.1)	(15.9)	<-50°	<10.8	$CDCl_3$
2b	36.8	14.4	>174	>22.2	$CHCl_2CHCl_2$
3a	12.1	14.3	-50	11.0	$CDCl_3$-CS_2
3b	40.9	14.3	164	21.7	C_4Cl_6

in 2a is fast. On raising the temperature, the AB quartet of 2b in tetrachloro-ethane gradually broadened but the coalescence of the signals was not observed up to 174°C. By a similar examination of the ^{1}HNMR spectra of 3b at various temper-atures, the coalescence temperature Tc of the quartet due to the benzylic protons
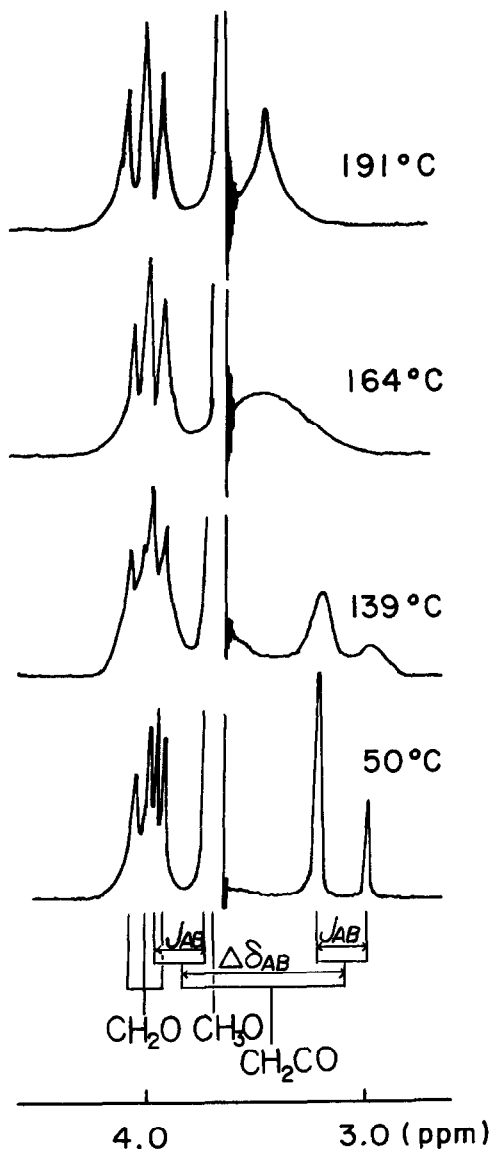

Fig. 1. Temperature dependence of the ^{1}HNMR (60 MHz) spectra of 3b in C_4Cl_6.

was found to be 164°C. In the case of 3a, however, the Tc was -50°C. Chemical shifts and coupling constants were measured at -70°C, where, the signals being sharp, the exchange of protons could be neglected.

The free energies of activation were obtained by putting the NMR parameters into the equation[6]

$$\Delta G_C^{\ddagger} = 4.57 Tc \left\{ 9.97 + \log_{10}(Tc/\sqrt{\Delta\delta_{AB}^2 + 6J_{AB}^2}) \right\}$$

and the results are summarized in Table 1.

It is immediately pointed out that the compounds carrying methoxyl groups show higher free energy of activation than those carring methyl groups by 10 kcal/mole or more. This large difference in the energy of activation must be attributed to the presence of methoxyl groups instead of the methyls because the other part of the molecule is the same.

The methoxyl groups in 2b and 3b will be in the plane of the benzene ring, at the ground state as are known in the case of p-dimethoxybenzene.[7] The methoxyl groups may or may not be coplanar with the aromatic ring at the transition state, but, in either case, the barrier to rota-tion of the benzene ring will be high because the methoxyl group is bulkier in

the coplanar conformation and because the energy is needed to twist the methoxyl group out of the plane of the benzene ring in addition to the fact that the methoxyl group is still bulkier in that conformation than the methyl.

To our knowledge, this is the first example of materializing that the methoxyl group is really bulkier than the methyl group under suitable conditions

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