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Nonplanar Cyclobutane. I. The 3-Isopropylcyclobutyl System. Nuclear Magnetic Resonance Spectra of Alcohols and Amines[1]

Sir:

During the past 15 years, a good deal of physical information has accumulated which supports a nonplanar structure for cyclobutane.[2–6] Recently, chemical evidence for a folded conformation for the cyclobutane system has been adduced from equilibration data.[7]

Cyclobutane is quite flexible and exhibits a dynamic ring-bending equilibrium which has been termed "pseudo-rotation.[8] In a pair of conformers representing the extremes of such flexion, equatorial and axial configurations may be assigned to substituents.[9] We have attempted to utilize a bulky group in a 1,3-disubstituted cyclobutane to retard this equilibrium to delineate these positions better in a manner analogous to the effect of "holding" groups in the cyclohexane system.[10] Thus, in Figure 1, favored conformations appear on the left. We hoped in this fashion to probe possible differences in behavior between axial and equatorial substituents, perhaps paralleling differences in cyclohexanes, and to provide better definition of the condition of nonplanarity. Accordingly, we have prepared and examined a series of 3-isopropylcyclobutane derivatives. In this communication, we wish to present the nmr spectra of the isomeric 3-isopropylcyclobutanols and 3-isopropylcyclobutylamines[11] (Figures 2 and 3), which provide convincing and dramatic evidence for the model depicted.

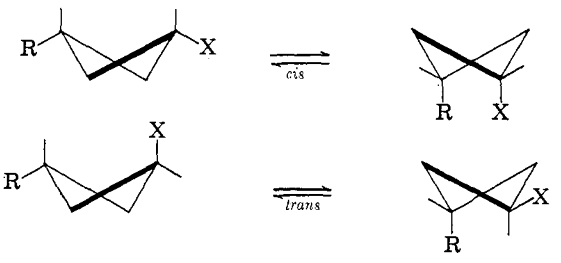

Figure 1.

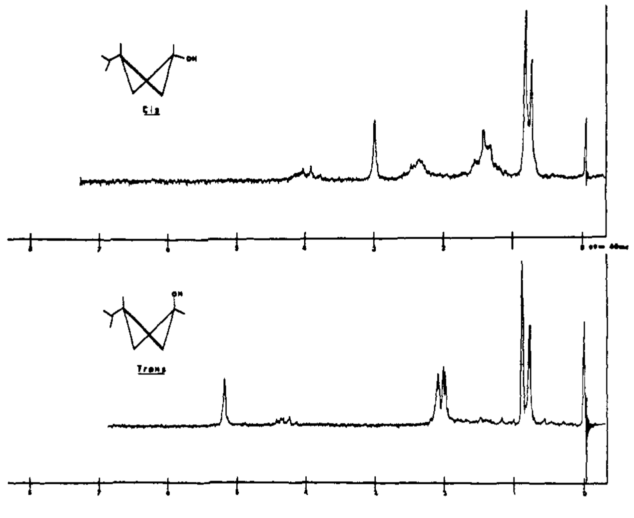

Figure 2.

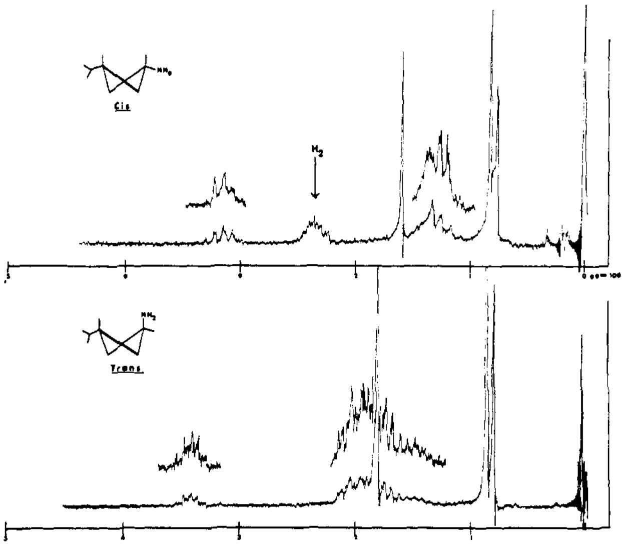

Figure 3.

The spectra were recorded for the amines at 100 Mc and the alcohols at 60 Mc. In both sets of spectra, the unsymmetrical doublet of the methyl protons appears similarly centered at *ca.* 0.8 ppm (relative to TMS). In the amines, the amino protons may be seen as a sharp resonance at about 1.6 ppm for the *cis* and 1.8 ppm for the *trans* isomer. The proton geminal to the amino group is located as a multiplet centered at 3.2 ppm for the *cis* and 3.4 ppm for the *trans* isomer. The latter assignment is reasonable since these protons are the most strongly deshielded by the amino group and should appear at lowest field. This conclusion was verified by a double resonance experiment which showed this resonance coupled to the resonances centered at 2.3 and 1.3 ppm in the *cis* and at 1.9 ppm in the *trans* isomer. The latter resonances are due to the ring methylene protons, and it is here that a pronounced distinction between the *cis* and *trans* isomers is seen.

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(11) Full details of the synthesis and configurational assignments of the alcohols and amines will be published in a forthcoming paper concerned with deamination of the amines.

A quite similar situation exists for the alcohols. The OH proton appears at 3.1 ppm for the *cis* and at 5.2 ppm for the *trans* isomer; the proton geminal to the OH is centered at 4.1 ppm for the *cis* and 4.3 ppm for the *trans* isomer. Ring methylene protons are centered at 2.4 and 1.4 ppm for the *cis* and at 2.1 ppm for the *trans* isomer. In the alcohols, as determined by relative integrated peak areas,[12] remaining tertiary protons of the isopropyl group and C_3 appear overlapped by the high-field methylene resonances. The same situation was observed in the amines.

If our conformational picture of cyclobutane is a reasonable one, analogies with nmr effects in cyclohexane should be valid. The large variance between the *cis* and *trans* ring methylene signals is strongly reminiscent of the "axial effect" observed in the cyclohexanes.[13–17] It has been observed in several instances that axial substituents cause a narrowing and intensification of the resonance due to equatorial and axial ring protons. Such cases as OH in the decalins[16] and steroids[18] and alkyl groups in cyclohexanes[19] are illustrative.

Equatorial protons ordinarily absorb at lower field than axial protons in cyclohexane. This distinction is actually seen only in temperature-frozen or conformationally homogeneous (*i.e.*, *t*-butylcyclohexane[20]) systems, since ring equilibration causes averaging. If, in a homogeneous disubstituted system, the shielding effects of substituents on axial *vs.* equatorial protons were disparate but unopposed, one would expect broadening of overlapping resonances or even separation, whereas opposition would result in narrowing of the signal. Equatorial alkyl groups have been shown to shield *cis* (axial) adjacent protons more strongly than *trans* (equatorial),[19] while axial substituents (including OH and alkyl) shield *cis* (equatorial) adjacent protons and deshield *trans* (axial) adjacent protons.[18,19] Thus, in the *trans* 3-isopropylcyclobutane isomers, with predominantly equatorial isopropyl and axial OH or NH_2 expected, effects are opposed, resulting in resonance narrowing and overlapping for the ring methylene signals. In line with previous reasoning, in the *cis* isomers equatorial OH or NH_2 groups, which are strongly electronegative, must deshield *trans* (equatorial) more than *cis* (axial) ring protons, so that the equatorial protons more strongly deshielded by equatorial OH or NH_2 appear further downfield than the axial protons more strongly shielded by the equatorial isopropyl group. A similar effect may be noted in *trans*-4-*t*-butyl- and *cis*-3-*t*-butylcyclohexylamine, which possess equatorial NH_2 groups and two separate ring methylene signals, whereas their isomers have single more intense bands at intermediate field.[15] We have likewise observed an analogous but much less pronounced effect in the 3-isopropylcyclobutanecarboxylate esters.[21]

The present results are therefore intelligible only in terms of a relatively homogeneous nonplanar system containing predominantly or exclusively equatorial isopropyl and axial or equatorial OH or NH_2. The equilibrium depicted in Figure 1 must lie substantially to the left for both sets of isomers. We believe this to be the first instance of the successful use of a holding group in cyclobutane. A sound basis is thus at hand for further investigations of conformational distinctions in this system.

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[12] Relative areas going upfield: *cis* OH, 1:1:2:4:6; *trans* OH, 1:1:6:6; *cis* NH_2, 1:2:6:6, *trans* NH_2, 1:8:6.

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[22] Based in part on the dissertation submitted by R. A. Doughty to the Graduate School of the University of Miami in partial fulfillment of the requirements for the Ph.D. Degree in chemistry.

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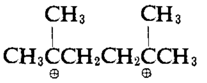
Stable Carbonium Ions. XXXII.[1] Alkyldicarbonium Ions

Sir:

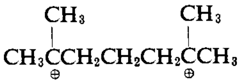
Recently we reported the direct observation of alkylenedioxodicarbonium ions (acyl dications).[2] No observation of alkyldicarbonium ions has yet been reported.

We now wish to report the direct observation of the first stable alkyldicarbonium ions. When 2,5-dichloro-2,5-dimethylhexane[3] and 2,6-dichloro-2,6-dimethylheptane[4] were dissolved in SO_2–SbF_5 solution at low temperature, clean, slightly colored solutions resulted which gave the spectra shown in Figures 1 and 2. These spectra are those of the dicarbonium ions I and II, respectively, in the form of the di-SbF_5Cl^- salts.



$CH_3\underset{\oplus}{\overset{CH_3}{C}}CH_2CH_2\underset{\oplus}{\overset{CH_3}{C}}CH_3$

I



$CH_3\underset{\oplus}{\overset{CH_3}{C}}CH_2CH_2CH_2\underset{\oplus}{\overset{CH_3}{C}}CH_3$

II

The dication nature of these ions was deduced from three observations: (1) the nmr spectra, indicative of the ions, in particular the downfield shifts of the methyl and methylene groups adjacent to the positively charged carbon atoms;[5] (2) the long-range coupling of the methyl groups with the adjacent methylene groups through the sp^2 center;[5,6] and (3) the isolation of dimethyl ethers on quenching solutions of the dications in methanol at −78°.[7]

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