interesting solvent shift for two mixtures of the TFA esters of *cis*- and *trans*-4-*t*-butylcyclohexanol.[7]

For a single unknown alcohol or a mixture of alcohols our operational procedure consists of TFA preparation, dissolution in a solvent if necessary, addition of a small amount of ethyl trifluoroacetate as an internal reference, and recording of the spectrum. Ethyl trifluoroacetate is a reliable internal standard because at 56.4 Mc all other primary TFA's are downfield (2–17 cps), all phenol TFA's downfield (30 cps or more), all secondary TFA's upfield (3–15 cps), and all tertiary TFA's upfield (30–36 cps).

We do not wish to claim that the trifluoroacetylation–^{19}F nmr technique is in every case the simplest and best means of characterizing hydroxyl groups. There will certainly be instances where other techniques are adequate. However, the method described here does have certain obvious advantages. First, with this method, one is looking at the signal from three ^{19}F nuclei *vs.* one ^{1}H nucleus (as in the case of several other recently described nmr techniques) which can be a multiplet.[8] Thus, at worst, a signal to noise increase of around 2.5 should be realizable. In addition, because one observes the ^{19}F spectrum, signals from the other protons in the molecules of interest are far removed and the restrictions on the choice of solvent are essentially removed.

(7) Although chemical shift concentration and solvent effects have been observed, so far for mixtures of TFA's chemical shifts are always in the order of shielding primary < secondary < tertiary. Comparison of the data in Figure 1 for the chemical shifts in parts per million for the TFA's of *cis*-4-*t*-butylcyclohexanol (A) (75.09) and *trans*-4-*t*-butylcyclohexanol (B) (74.99) with those of 2-methyl-2-butanol (C) (74.99) and *t*-butyl alcohol (D) (75.05) would seem to refute this statement. However, this is an example of the concentration effects. In one case (Figure 1d) the solution was 5% in ester and in the other case (Figure 1a) 20% in ester. In a 20% ester mixture of DMSO (7% CCl$_3$F) A, B, C, and D show chemical shifts of 74.57, 74.69, 75.00, and 75.06 ppm, respectively.

(8) As can be seen in the spectra shown above and more readily in spectra recorded at slightly slower sweep rates, there exist small splittings (0.15–0.30 cps) of the CF$_3$ groups with the proton(s) five bonds removed.

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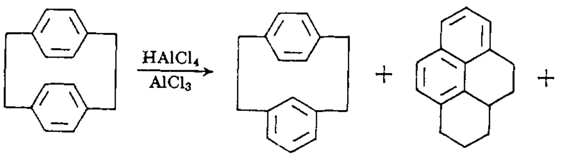
[2.2]Metaparacyclophane, a Highly Strained Ring System[1]

Sir:

Treatment of powdered [2.2]paracyclophane[2] (I) with a solution of dry methylene chloride saturated with hydrogen chloride and aluminum chloride at 0° for 30 min produced [2.2]metaparacyclophane[3] (II) in 44% yield, 1,2,2a,3,4,5-hexahydropyrene[3] (III) in 10% yield, bibenzyl (IV) in trace amounts, and a 7% yield of starting material. These products were isolated by preparative vpc on a 20% Epon 1001 on Firebrick column at 165° under 15 psi of helium, and they exhibited the following retention times: I, 63 min, mp 285–287°, undepressed by admixture with authentic material; II, 48 min, mp 81–81.5°; III, 128 min, mp 102.5–103.3° (lit.[4] 103–105°); IV, 15 min, mp 49–50°, undepressed upon admixture with an authentic sample.



I II III

$(C_6H_5)_2CH_2$
IV

The structure of [2.2]metaparacyclophane was assigned on the basis of its combustion analysis,[3] degradation products, and nmr (in carbon tetrachloride) and ultraviolet absorption spectra (in 95% ethanol). Reduction of II with potassium metal in dimethoxyethane produced *m,p'*-dimethylbibenzyl (V), an oil,[3] which when oxidized with potassium permanganate gave a mixture of isophthalic and terephthalic acids, identified by the retention times of their dimethyl esters on vpc.[5] The ultraviolet (Figure 1) and nmr spectra of V support the assigned structure. The former exhibits bands expected from a mixture of *m*- and *p*-xylenes. The latter gave the following bands: eight protons centered at τ 3.05 (four protons as a singlet at τ 3.03 assigned to the *para*-disubstituted benzene ring and four protons at τ 3.06 (partially masked by the above peak and possessing a typical *meta* splitting pattern assigned to the *meta*-disubstituted benzene ring); four protons as a singlet at τ 7.22 (methylene protons); six protons as a singlet at τ 7.74 (methyl protons). Direct oxidation of [2.2]metaparacyclophane with potassium permanganate gave the expected isophthalic and terephthalic acids.[5]

The nmr spectrum of [2.2]metaparacyclophane (II) strongly supports the assigned structure. Although protons a and b are shielded by the ring currents of the transannular aromatic nuclei, the effect is considerably less than that observed for the two protons that correspond to a in [2.2]metacyclophane[6] (τ 5.73). The ultraviolet spectrum of II (Figure 1) is strikingly different from that of the open chain model (V). The cycle exhibits a new and intense band at ~240 mμ which is not far from the 244 mμ band of [2.2]paracyclophane which was attributed to mixing of transannular charge transfer with normal excited states.[7] The remnants of the fine structure in the spectrum of the open-chain model are visible in that of the cycle (II) in the 260–280 mμ region. The bands at 283 and 291 mμ in the spectrum of the cycle are absent in that of the open-chain compound and are probably associated mainly with a serious deformation of the *para*-substituted benzene ring from its normally planar configuration. Molecular models suggest that this deformation is much greater than that in [2.2]paracyclophane, whose side-chain substituted aromatic carbon atoms are bent out of the plane of the other four aromatic carbon atoms by 13°. That such bending causes bathochromic

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(1) The authors wish to thank the National Science Foundation for a grant used in support of this research.

(2) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

(3) Combustion analysis gave carbon and hydrogen values less than 0.2% from theory.

(4) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(5) D. J. Cram and H. P. Fischer, *J. Org. Chem.*, **30**, 1815 (1965).

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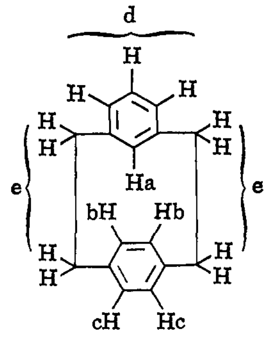
(7) R. C. Helgeson and D. J. Cram, *ibid.*, in press.



II

Ha, broad singlet (1 proton) at τ 4.76; Hb, doublet (two protons), centered at τ 4.30 ($J \sim 1.9$ cps); Hc, doublet (two protons), centered at τ 3.03 ($J \sim 1.9$ cps); Hd, multiplet (three protons), centered at τ 3.37; He series of multiplets (eight protons), ranging from τ 6.88 to 8.13.

shifts has been well established.[8] Allinger, *et al.*,[8b] predict that [7]paracyclophane should have a long-wavelength absorption band at 288 mμ and that the 1,4-carbon atoms are bent out of the plane of the other four by about 26°. The question of whether the band at 291 mμ in the spectrum of II is the predicted absorption is a matter for conjecture.

The long-wavelength charge-transfer band in the visible spectrum of the tetracyanoethylene π salt of II in methylene dichloride occurred at 455 mμ. This transition is of higher energy than that of any of the other paracyclophanes[9a] and is between that of *m*-xylene (440 mμ) and *p*-xylene (460 mμ).[9b] This fact implies that II is a weaker π base than either [2.2]-paracyclophane (π salt, $\lambda_{\max}$ 521 mμ)[9a] or [2.2]metacyclophane (π salt, $\lambda_{\max}$ 486 mμ).[10]

The structure of hexahydropyrene III was assigned on the basis of its combustion analysis,[3] melting point,[4] the melting point of its orange picrate (150.4–150.6°, lit.[4] 147–148°), its vpc retention time (close to that of pyrene), the similarity of its ultraviolet spectrum to that of alkylated naphthalenes, and its nmr spectrum in carbon tetrachloride. The five aromatic protons occurred as a multiplet centered at τ 2.82; the five benzylic protons as a multiplet extending from τ 6.75 to 7.5; the six methylene protons as a multiplet extending from τ 7.65 to 8.95.

Two possible driving forces are envisioned for the rearrangement of I to II. Compound I has about 31 kcal/mole strain energy,[11] much of which is probably associated with π–π repulsion. In the conversion of I to II, the rings are decentered and π–π repulsions decreased. Although one of the two benzene rings of II (*para*-substituted) is probably more deformed than the two rings of I, the other (*meta*-substituted) is probably less deformed, and the over-all deformation strain of the two systems might be comparable.

The second driving force for rearrangement could derive from the facts that *m*-dialkylbenzenes are stronger bases toward protons than *p*-dialkylbenzenes,[12] and that the conjugate acid of II is of lower energy than that of I. The highly colored reaction mixtures suggest the presence of these conjugate acids. Production of hexahydropyrene III probably occurs through [2.2]-metacyclophane as an intermediate, which when treated with aluminum chloride is known[4] to produce III. A trace of [2.2]metacyclophane has been detected in the reaction mixture for rearrangement by vpc and nmr methods, but the substance occurs in too small an amount to be isolated. Acid-catalyzed rearrangements of methylene groups in paracyclophane systems have been observed previously,[13] particularly in strained systems.

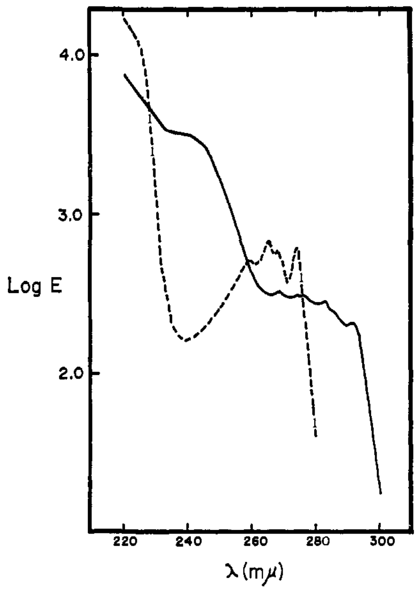
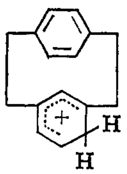


Figure 1. Ultraviolet absorption spectra (Cary Model 14 spectrophotometer) in 95% ethanol: [2.2]metaparacyclophane (II), ———; *m,p'*-dimethylbibenzyl (V), ----.

The chemistry of [2.2]metaparacyclophane is under active investigation.



conjugate acid of II

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[8] (a) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961), and earlier papers; (b) N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Am. Chem. Soc.*, **85**, 1171 (1963); (c) E. M. Arnett and J. M. Ballinger, *Tetrahedron Letters*, 3803 (1964).

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[10] The authors wish to thank Dr. N. L. Allinger for a sample of [2.2]metacyclophane.

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[13] B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, p 245.

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Toward a Better 2pπ-Atomic Orbital for π-Electron Theory[1]

Sir:

The concept of a carbon 2pπ atomic orbital (AO) plays a key role in the theory of the electronic structure

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