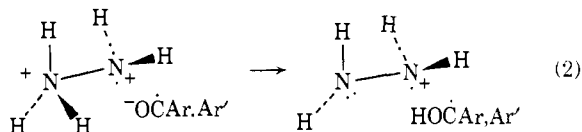


ylated hydrazines will be examined at lower pH, but systems are needed in which the ketone remains soluble in acid medium.

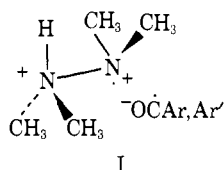
Tetramethylethylenediamine behaves like a normal photoreducing agent, similar to triethylamine, $\phi \sim 0.7$, and monoprotonation leads only to the increase in quantum yield due to the change in reduction product. The result with triethylamine is of interest since protonation, which might make the n electrons unavailable, appears to decrease quantum yield only moderately, to 0.35. The electrophilic excited ketone may react with the triethylammonium ion, displacing the proton, but less efficiently than it displaces the hydrogen bond of water. The bicyclic diamine DABCO is an effective quencher, $k_{ir} = 1.69 \times 10^8 M^{-1} \text{sec}^{-1}$, and a most inefficient reducing agent, both as the free base at pH 12 and in the monoprotonated form at pH 7.

The free hydrazines and DABCO readily form the charge transfer complexes, and these may be highly stabilized by interaction between the orbitals of the unpaired and the lone pair electrons in the cationic moiety.⁸ Spin inversion and quenching may occur before hydrogen transfer. It is possible but less likely that reversible hydrogen transfer accounts for quenching by the hydrazines. DABCO is a photoreducing agent for *p*-aminobenzophenone^{1b} and for benzophenone in hydrocarbon solvents where the CTC may not be excessively stable and thus not lead to quenching. It will be of interest to study photoreduction by hydrazines in nonpolar solvents.

In the monoprotonated hydrazines interaction begins at the nonprotonated n -electrons; the additional partial positive charge increases acidity and facilitates proton transfer from the protonated N, leading to reduction, eq 2. Interac-



tion with monoprotonated DABCO may occur similarly at the neutral N, but the geometry may lead to discharge of the proton to the solvent water, and quenching, as by the unprotonated base. Similarly protonated tetramethylhydrazine may lead largely to quenching if the CTC has I as its dominant conformer and the proton is transferred to water rather than to the ketyl radical anion. Transfer of proton to



water and quenching may be competitive with reduction in the reaction of eq 2 also. Transfer of an acidic proton from the γ -atom (oxygen) of a CTC in a noncyclic system in nonpolar solvent has been proposed in the benzophenone photosensitized decarboxylation of carboxylic acids⁹ and in the photosensitized fragmentation of 2-anilinoethanols.¹⁰ The importance of the basicity of the anionic part of the CTC has also been noted.⁴ The proper juxtaposition of groups which may separately transfer an electron and a proton may be an important property of biological redox systems.

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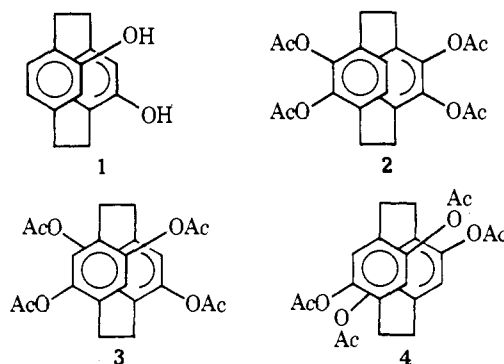
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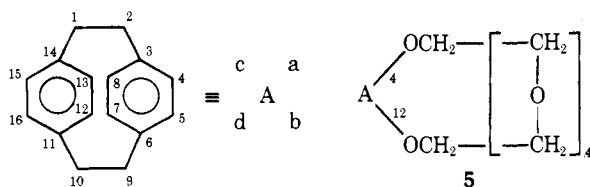
The [2.2]Paracyclophanyl Group as a Structural Unit in Host Compounds¹

Sir:

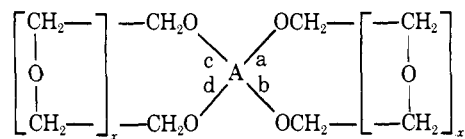
Former papers in this series demonstrated how the 1,1'-binaphthyl group incorporated into cyclic polyethers provided host compounds with chiral recognition in complexation of primary amines,^{2a} amino acids,^{2b} and amino esters.^{2c} This group also provided sites for attachment of arms terminated in functional groups that extended around, over, or under the central hole of the cycles.^{2b-e} The [2.2]paracyclophanyl group provides advantages as a shaping unit in host compounds. (1) The parent compound contains 16 potentially substitutable sites (eight aromatic and eight aliphatic) for its incorporation into large multiheteromacrocycles and for providing additional functionality. (2) The rigidity of the hydrocarbon system fixes the positions of attached chains relative to one another. (3) The symmetry properties of the system are highly manipulable.³ This paper describes the synthesis of a variety of host compounds containing this unit.



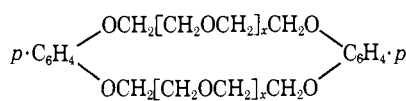
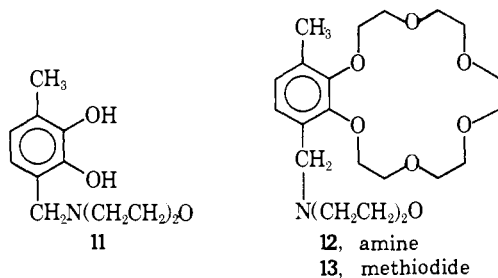
Diol **1**⁴ with pentaethylene glycol dichloride in 1-butanol-potassium hydroxide (reflux, 24 hr) gave 18% of **5**⁵ after chromatography on alumina, mp 73–74°. Tetraacetate **2**⁵ (mp 340° dec, 20%) was prepared by treating 3,6-bis(bromomethyl)catechol diacetate⁶ with sodium iodide in refluxing 2-butanone.⁷ Tetraacetates **3**⁵ (mp 263–264°, 25%)^{7b} and **4** (mp 283–284°, 5%)^{7b} were similarly obtained^{7a} from 2,5-bis(bromomethyl)hydroquinone diacetate⁶ (separated on silica gel, benzene-chloroform). These three tetraacetates were each reduced with lithium aluminum hydride (soxhlet extraction by tetrahydrofuran), and the corresponding tetrols were used directly in ring closures without characterization.⁸ Multiheteromacrocycles **6–10** were prepared from these tetrols and tetraethylene or pentaethylene



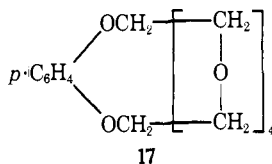
[2.2]Paracyclophane



	a	b	c	d	x	Mp (°C)	Yield (%)
6^s	4	5	15	16	3	192-193	6
7^s	4	5	15	16	4	157-158	14
8^s	4	12	7	15	3	118-119	3
9^s	4	12	7	15	4	121-122	25
10^s	4	13	7	16	4	133-134	23



	x	Mp (°C)	Yield (%)
14^s	2	96-97	7
15^s	3	93-94	8
16^s	4	67-69	7



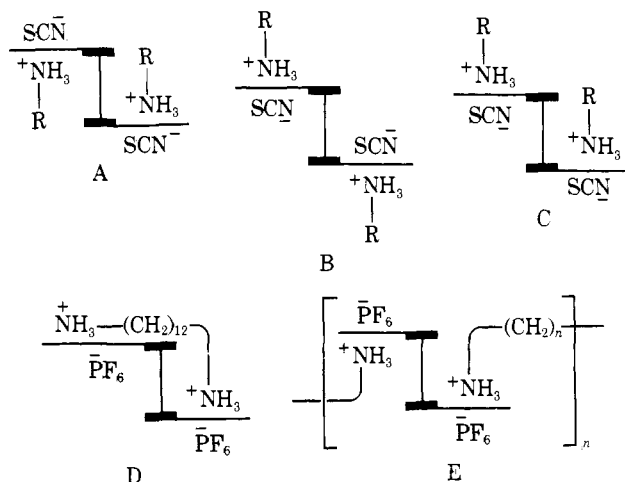
glycol dichlorides or ditosylates in either 1-butanol-potassium hydroxide or tetrahydrofuran-potassium hydroxide under conditions that carefully excluded oxygen.

In the above synthesis of **7**, the cyclophane ring system was first assembled, and then the heterocycle. In an alternative synthesis, the order was reversed. A Mannich reaction applied to 1,2-dihydroxy-3-methylbenzene gave compound **11^s** (83%, mp 134-135°), which with pentaethylene glycol dichloride and potassium *tert*-butoxide in tetrahydrofuran gave **12^s** (35%) as an oil. Methiodide **13^{sa}** was prepared (oil) and converted to its hydroxide, whose aqueous solution was azeotropically distilled with toluene (10 hr) in the presence of phenothiazine⁹ to give **7** (10%), identical (mp, tlc, pmr) with the sample of **7** prepared by the other route.

Model cycles **14-16** were prepared from hydroquinone and triethylene, tetraethylene, and pentaethyleneglycol ditosylates, respectively, in tetrahydrofuran-potassium *tert*-butoxide (reflux, 24 hr). The dimeric products moved slower on alumina chromatograms (chloroform-ether) than the monomeric compounds. Of the latter, only **17^s** was characterized (oil).

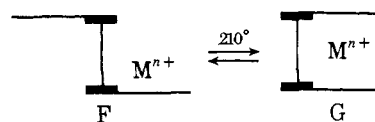
Cycle **7** formed (80%) a crystalline one-to-two complex^{5a,b} (**18**) with *tert*-butylammonium thiocyanate (from

chloroform and ethyl acetate), mp 125-127°. Since **7** has sidedness, **18** could have the three possible structures symbolized by A, B, or C. Of these, molecular models (Corey-Pauling-Koltun) suggest that A is the most likely structure for **18** due to sterically enforced conformations of the ArOCH₂ groups. This hypothesis was strengthened by the fact that one-to-one complexes^{5a,b} crystallized from chloroform when either hexamethylenediammonium or decamethylenediammonium hexafluorophosphates were mixed with **7**. The hexamethylene complex must be polymeric since the hexamethylene unit is too short to span the distance between the two macrorings. The decamethylene unit is long enough (molecular models), but only if: (1) the chain goes over the face of the benzene ring as in D, which should move the middle protons upfield in their pmr spectra; (2) the outside face of one macroring is complexed. The pmr spectrum of the complex is normal, suggesting that the decamethylene complex too is polymeric as in E. Hosts **9**



and **10** were both found to solubilize, in CDCl₃, 2 mol of solid *tert*-butylammonium tetraphenylborate that were insoluble in the absence of cycle. Whereas **9** is chiral, possesses the unusual D₂ symmetry, and is not sided, **10** is achiral, sided, and, in principle, could form three different two-to-one complexes (as with **7**). Unlike the complexes of **7** and **10**, those of **9** move the aromatic proton upfield in the pmr spectrum (by 0.28-0.5 ppm) as compared to noncomplexed host in CDCl₃. Cycles **14**, **15**, and **16** were found (pmr) to extract into CDCl₃ 0.14, 0.60, and 0.92 equiv, respectively, of α -phenylethylammonium thiocyanate (out of 6) per equivalent of cycle from D₂O (equal volumes) at 25°. Molecular models suggest that of the three, host **16** offers the most and best arranged binding sites to guest alkylammonium ions. The binding constants of these and other host compounds are reported elsewhere.¹⁰

Attempts to thermally isomerize¹¹ and stabilize the relatively unstable syn isomer of **7** by preferred complexation failed (F \rightleftharpoons G). In these experiments, Mⁿ⁺ was hydrazine sulfate or potassium or cesium acetate.



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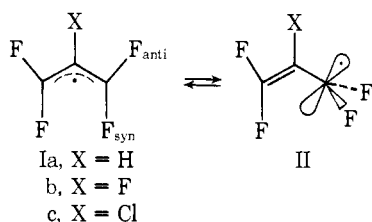
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An Electron Spin Resonance Study of the Stereomutation in 1,1,3,3-Tetrafluoroallylic Radicals

Sir:

It is well known that simple allylic radicals are remarkably stable toward geometrical isomerization.¹ In a recent high-temperature esr study, we have shown that the allyl radical is static on the esr time scale even at 280° precluding a ΔG^* for internal rotation of less than 17 kcal/mol.² We wish to report now that the replacement of the terminal protons in the allyl radical by fluorines markedly increases the rate of internal rotation about the allylic bonds.³ We find, furthermore, that halogen substituents in the 2 position (Ib, c) further decrease the activation energy to internal rotation ($\text{Cl} > \text{F}$). The latter effect is a manifestation of radical stabilization in β -haloalkyl radicals which is a topic of lively current interest.⁴



The 2-chlorotetrafluoroallyl radical Ic was generated photochemically in a cyclopropane-ethane solution from 2-chloro-3-bromotetrafluoropropene by reaction with tri(*n*-butyl)silyl radicals as bromine abstracting agents.⁵ At -52° the esr spectrum consists of a quintet of 43.3 G without resolvable Cl hyperfine structure indicating four equivalent fluorines on the esr time scale. Lowering the temperature produces two types of line shape effects: first, a strongly viscosity-dependent broadening of all lines except the central peak and, second, an additional broadening of the $M_I = \pm 1$ and $M_I = 0$ lines. The first effect is related to the modulation of the large anisotropic component of the fluorine hyperfine A tensor by molecular tumbling (dipolar broadening)⁶ while the second is caused by a slowing of the exchange of the terminal fluorines. The latter is complete at

-102° with the evolution of a triplet-of-triplets spectrum appropriate for two pairs of inequivalent fluorines. A fitting of the spectra by density-matrix line shapes calculations⁷ based on noncorrelated exchange of the two pairs of syn and anti fluorines indicates a rate of $3 \times 10^7 \text{ sec}^{-1}$ at -80° and a ΔG^* of 4.5 kcal/mol for the exchange process.

The esr spectra of Ib (Figure 1) and Ia (Table I) can be obtained by the same method and are similarly temperature dependent. Fluxional spectral behavior, however, occurs at higher temperatures. A line shape analysis leads to Arrhenius plots from which activation free energies of 6.1 and 7.2 kcal/mol, respectively, can be extracted.

A mechanism for stereomutation based on a concerted exchange of the terminal fluorines brought about by disrotatory or conrotatory motion of the $-\text{CF}_2$ termini concomitantly with the closing of the $\text{C}_1\text{C}_2\text{C}_3$ angle cannot be excluded *a priori*. Calculated spectra for this mechanism do show a different evolution of the line shapes but the differences can easily be confused with the effects of dipolar broadening. The observation of the isomeric 2,2,3,3-tetrafluorocyclopropyl radicals from the corresponding bromides,⁸ however, militates against such mechanism.

INDO calculations⁹ for the coplanar perfluoroallyl (Table II) predict remarkably well the isotropic coupling constants for the terminal fluorines. The agreement is less satisfactory for F_2 although the *negative* sign for this coupling is in fact borne out by the experimental temperature dependence of its magnitude (Table I). Since the vibronic contribution to this coupling should become more positive as the temperature increases, owing to larger amplitudes for out-of-plane motions and hence increased possibilities for direct spin delocalization, the observed decreasing magnitude of $a(\text{F}_2)$ with increasing temperature clearly demands a negative sign for this coupling in the ground vibronic state. The calculations also predict a substantial unpaired spin density in the p_z orbitals on the terminal fluorines (19%) indicating an extension of the π allylic MO system over these fluorines. This result is consistent with the large anisotropy of the A tensor inferred above from the pronounced dipolar line broadening effects.

The dramatic lowering of the rotational barriers in these radicals relative to the allyl radical itself is not entirely un-

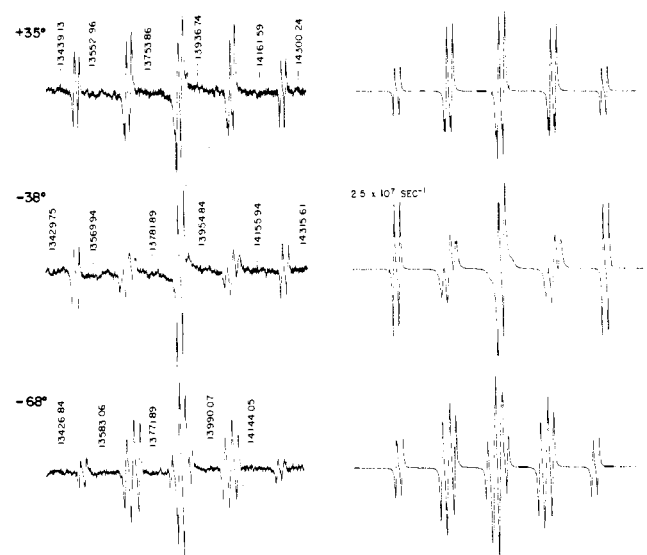


Figure 1. ESR spectra of the perfluoroallyl radical in cyclopropane. The calculated spectra (density matrix including higher order effects) refer to three conditions for the nonconcerted exchange of the terminal fluorines: fast exchange (top), $k = 2.5 \times 10^7 \text{ sec}^{-1}$ (middle), and slow exchange (bottom).