sis, prepared by a second crystallization from the same solvent mixture, melted at 115–116°.

Anal. Calcd for $C_{12}H_{18}N_2S$: C, 64.82; H, 8.16; N, 12.60; S, 14.42. Found: C, 64.74; H, 8.23; N, 12.55; S, 14.41.

The picrate of this imine after two crystallizations from ethanol melted at 154–155°.

Anal. Calcd for $C_{17}H_{20}N_4O_7$: C, 52.04; H, 5.14; N, 14.28. Found: C, 52.10; H, 5.25; N, 14.25.

2-Substituted-2-cyclohexen-1-imine Hydrothiocyanate.—2-Cyclohexen-1-one and carvone were treated, in refluxing toluene, with 1 mole equiv of ammonium thiocyanate as described above. One mole equivalent of water separated and oily imine hydrothiocyanates were formed. They could not be purified either by crystallization, distillation, or chromatography. They are yellow oils showing the three characteristic infrared peaks in the 2050–1610-cm^{-1} region, and are water soluble.

2-Phenyl-2-cyclohexen-1-one, prepared according to the literature[13] and treated with 1 mole equiv of ammonium thiocyanate in refluxing toluene, did not give any condensation product and was recovered unchanged from the toluene reaction mixture.

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Paracyclophane Phenols and Derivatives. I. The Synthesis and pK_A Values of 4-Hydroxy- and 4-Amino[2.2]paracyclophane

B. E. Norcross, D. Becker,[1] R. I. Cukier,[1] and
R. M. Schultz[1]

*Department of Chemistry, State University of New York,
Binghamton, New York 13901*

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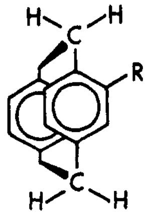
In connection with a continuing study of the Claisen rearrangement, we have had occasion to investigate the synthesis and reactivity of the phenol (**1**) and aromatic amine (**2**) derived from [2.2]paracyclophane. It soon became apparent that the chemical reactivity of these substituents was extensively modified by the uniquely strained nature of the aromatic ring to which they were attached.[2] In order to define these modified reactivities more quantitatively, the pK_A values of the phenol and the protonated amine (**3**) were determined, and are reported here. Since the general synthetic route used in this study varies extensively from other entries into this series,[3] the experimental details are reported in full.



1, R = OH
2, R = NH_2
3, R = NH_3^+

The pK_A measurements were made in an aqueous solution containing 5 wt % methanol. When compared to appropriate model compounds (Table I), these values reveal two major points: (1) the acid dissociation constant of the small linear substituent, OH,[4] on the [2.2]paracyclophane nucleus, primarily reflects the loss of resonance stabilization of the anion due to the bent nature of the adjacent benzene ring,[5] (2) the pK_A of the protonated anilium analog is apparently affected by at least two factors operating in opposite directions.[6]

TABLE I

pK_A VALUES

Compound	Solvent system[a]	pK_A	Ref
Phenol	H_2O	9.90	*b*
2,5-Dimethylphenol	H_2O	10.01	*b*
4-Hydroxy[2.2]paracyclophane	5% MeOH–H_2O	11.31	*c, d*
Aniline	H_2O	4.58	*e, f*
2,5-Dimethylaniline	H_2O	4.62	*e, f*
4-Amino[2.2]paracyclophane	5% MeOH–H_2O	4.43	*c, e, g*

[a] All measurements were made at 25.0°. [b] L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961). [c] This work. [d] Range is 11.225–11.426; *n* is 7; one standard deviation is 0.08 pK_A unit. [e] Protonated form. [f] T. W. Zawidzki, H. M. Papeé, W. J. Canady, and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1738 (1959). [g] Range is 4.314–4.496; *n* is 9; one standard deviation is 0.04 pK_A unit.

Two major factors affecting the change in pK_A of the protonated 4-amino[2.2]paracyclophane relative to an appropriately substituted unstrained aniline are the change in resonance stabilization due to the bent nature of the adjacent benzene ring, and changes in steric factors influencing ion and molecule solvation.

An estimate of the change in resonance interaction can be made from the data on the paracyclophanol, since steric differences are minimized with this substituent.[4] This resonance effect, operating "normally" with planar benzene rings, acts to stabilize the neutral aniline molecule relative to the ion, and thus is a factor increasing the acidity of the conjugate acid. Since this effect is diminished by the paracyclophane geometry, the resonance effect in the [2.2]paracyclophane system leads to decreased acidity of the conjugate acid, relative to the model compound.

It has been observed, that the steric hinderance in amines such as 2-methyl- and 2,6-dimethylaniline[7a] and 2,4,6-tri-*t*-butylphenylhydrazine[7b,c] manifests itself through a destabilization of the solvation of the ionic

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[1] American Chemical Society Petroleum Research Foundation Undergraduate Research Fellow.

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protonated form relative to the neutral molecule. Thus the steric effect operates to increase the acidity of the conjugate acid of amines. Changes on the order of 3 pK_A units in amine basicity have previously been attributed to this mechanism.[8] Since in the [2.2]-paracyclophane system the methylene bridge adjacent to the functional group is held much more rigidly in an unfavorable position relative to the large tetrahedral ammonium group than is the methyl group in the model compound, and it has been shown previously[7] that one *o*-methyl group does exert a significant steric effect, it is not unexpected that the paracyclophane geometry should result in a relatively large acid-strengthening influence attributable to steric effects on ion solvation. Since the pK_A values of the protonated model compound and 4-amino[2.2]paracyclophane are so nearly the same, it can be concluded that these opposing steric and resonance effects are nearly equal in their influence.

Experimental Section[9]

4-Nitro[2.2]paracyclophane.—In 580 ml of gently boiling glacial acetic acid, arranged for magnetic stirring in a 1-l., three-necked flask equipped with a reflux condenser, was dissolved 6.0 g (2.9×10^{-2} mole) of [2.2]paracyclophane[10] (complete solution requires about 45 min). In order to form a fine suspension, the solution was cooled rapidly to 70° with vigorous magnetic stirring. To this vigorously stirred suspension was added all at once 62 ml (1.6 moles) of fuming nitric acid. Stirring was maintained for 90 sec. The resulting yellow mixture was immediately poured onto approximately 2000 g of an ice–water mixture. After the ice melted, the resulting slurry was filtered through sintered glass. The yellow precipitate was taken up in chloroform and washed with water and saturated sodium chloride, and the resulting solution was evaporated to dryness. The yellow-orange semisolid was dissolved in a minimum of 40% chloroform in benzene, and chromatographed on a 110 × 50 mm column of Woelm neutral alumina, activity grade III (200 g), using the same mixed solvents as eluent. A first fraction of 175 ml was empty. The second fraction (130 ml) contained most of the 4-nitro[2.2]paracyclophane, mp 150–153°. Recrystallization of this material from ethanol yielded 2.78 g (38%) of light yellow needles, mp 155.0–157.0 (lit.[3a] mp 155.5–156.5°). Typically, an additional 0.2–0.4 g (~4%) of product was obtained from another 50–100-ml fraction of less pure material, and further chromatography–recrystallization treatment of the recrystallization mother liquor.

The proton magnetic resonance spectrum was consistent with that previously reported.[11] Medium to strong infrared bands were observed at 2920, 1512, 1340, 908, 875, 807, 702, 635, and 511 cm^{-1}.

4-Amino[2.2]paracyclophane.—A slurry of approximately 75 mg of 30% paladium-on-carbon catalyst[12] and 900 mg (3.55×10^{-3} mole) of finely ground 4-nitro[2.2]paracyclophane in 150 ml of methanol was treated in a Parr hydrogenator at room temperature and 50 psig of hydrogen for 2 hr. The resulting reaction mixture was filtered through a Celite filter pad and transferred, along with hot methanol washings of the filter pad, to a round-bottom flask, in which the total volume of solution was reduced to about 10 ml by use of a rotary evaporator. As the solution was reduced in volume, and cooled (toward the end of the evaporation process) by evaporation, granular crystals, varying in color from tan to light gray, were deposited. The supernatant, containing most of the impurities, was removed with a pipet, and the remaining crystals were washed several times with cold (−78°) methanol, and pumped to dryness. A first crop of 656 mg (83%) of 4-amino[2.2]paracyclophane was collected, mp 247–250° dec (lit.[3a] mp 239–241.5° dec). An additional 8% of pure amine was obtained by chromatography of the crude material in the methanol mother liquor, and washings on Woelm neutral alumina, grade III, using 10% diethyl ether in benzene as the eluent. The characteristic[11] proton magnetic resonance spectrum possessed peaks centered at $\delta = 2.95$ ppm (bridging methylenes), $\delta = 5.42$ ppm (orthohydrogen), and $\delta = 6.35$ ppm (other aromatic hydrogens). Medium to strong infrared bands were observed at 3460, 3380, 2920, 2850, 1615, 1500, 1425, 1285, 795, 715, 660, 590, and 510 cm^{-1}.

4-Acetoxy[2.2]paracyclophane.[3]—To a magnetically stirred solution of 1.5 g of sulfuric acid in 100 ml of water in a 250-ml beaker was added 1.6 g (4.75×10^{-3} mole) of 4-amino[2.2]-paracyclophane. The resulting slurry was purged with a slow stream of nitrogen for 10 min, then heated, with stirring and continued nitrogen purging, until solution occurred (solution was essentially complete after about 15 min at 85°). The pale blue solution was rapidly cooled with stirring, to −3 to −1°, during which time a flocculent, white precipitate formed. A solution of 1.0 g of sodium nitrite in 20 ml of water was added dropwise to diazotize the amine salt. Careful temperature control to maintain the range of −3 to −1° was essential. The diazotization was followed with starch-iodide paper, and required about 30 min to complete. The diazonium salt was not completely soluble under the conditions used, and so the resulting solution was a yellow slurry with a small amount of tan foam.

After the addition of nitrite, the nitrogen bubbler was removed, and a filtered solution of 10 g of sodium fluoroborate in 18 ml of water was added all at once to the diazonium solution. A change in slurry appearance was apparent. Stirring was maintained for 15 min, while the temperature was maintained between 10 and 15°. The resulting yellow diazonium fluoroborate salt was filtered rapidly and washed with a small portion of ice-water and with several portions of diethyl ether. The salt was dried in the filter by pulling air through it for a few minutes, then rapidly transferred to a cooled mixture of 8 ml of acetic acid and 11 ml of acetic anhydride.[13] (The salt cannot be allowed to come to room temperature, as decomposition to an intractable brown material readily occurs.) As soon as the exothermic solvolysis began, as evidenced by nitrogen evolutions and rapid temperature rise, the reaction mixture was cooled to keep the temperature in the region 25–35°. After 1–2 hr, the reaction mixture was quenched in 40 ml of an ice–water mixture. The resulting slurry was extracted with ligroin. The ligroin solution was washed with water and saturated sodium chloride solution, and taken to dryness. The resulting crystals were chromatographed on a 35 × 25 mm column of Woelm neutral alumina, activity grade III, using 50% benzene in petroleum ether (bp 66–75°) as eluent, and collected in 20-ml fractions. Fractions 2–6 contained a total of 716 mg of off-white crystals. Crystallization from *n*-hexane yielded 494 mg (41%) of white needles, mp 129–132°. Further chromatography and recrystallization of material from mother liquors produced an additional 90 mg (7%) of pure acetate. An analytical sample melting at 132.5–134.0° was obtained (lit.[3b] mp 132.5–133.5°). The pmr spectrum showed peaks centered at $\delta = 2.33$ ppm (methyl), $\delta = 3.08$ ppm (bridging methylenes), $\delta = 6.121$ ppm (orthohydrogen), and $\delta = 6.60$ ppm (other aromatic hydrogens). Medium to strong infrared bands occurred at 2930, 1750, 1370, 1215, 1105, 1090, 915, 795, 718, 645, and 515 cm^{-1}.

4 Hydroxy[2.2]paracyclophane.[3b]—A stirred solution of 556 mg (2.09×10^{-3} mole) of 4-acetoxy[2.2]paracyclophane in 150 ml of methanol was purged with nitrogen for 15 min. To this clear, colorless solution was added a solution of 5 ml of methanol containing one pellet of potassium hydroxide. The resulting light yellow solution was stirred for an additional 30 min at room

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[9] Melting points are uncorrected. Unless otherwise stated, infrared spectra were determined on pressed potassium bromide disks containing 1–3 wt % of sample, and were determined on a Perkin-Elmer 521. Ultraviolet spectra were determined on a Cary 14, and proton magnetic resonance was determined on a Varian Associates A-60, in deuteriochloroform, using tetramethylsilane as internal standard. Thin layer chromatography, performed on 250-μ-thick layers of silica gel containing a gypsum binder, was used to follow the course of all synthetic reactions. Pure compounds showed only one spot when chromatographed with various mixed solvents (generally ether–benzene), and developed with dilute alkaline potassium permanganate solution.

[10] Union Carbide Corp., Plastics Division, Bound Brook, N. J.

[11] L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963).

[12] Engelhard Industries, Inc., Newark, N. J.

[13] A. W. Burgstahler, P. Chien, and M. O. Abdel-Rahmar, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

temperature. The mixture resulting from quenching this solution with 75 ml of water was extracted with diethyl ether. The combined ether extracts were washed with water and saturated sodium chloride solution, dried, and taken to dryness under nitrogen. Evaporation of the ether solution under nitrogen provided 468 mg (100%) of 4-hydroxy[2.2]paracyclophane, mp 223–228° (sealed evacuated capillary) (lit.[3a] mp 225–229°). The nmr spectrum showed peaks centered at $\delta = 3.02$ ppm (bridging methylenes), $\delta = 4.45$ ppm (hydroxyl hydrogen), $\delta = 5.62$ ppm (orthohydrogen), and $\delta = 6.50$ ppm (rest of aromatic protons). Strong and medium peaks in the infrared spectrum were found at 3610 (CCl_4 solution), 2920, 1560, 1495, 1415, 1260, 1140, 1085, 975, 795, 715, 665, and 612 cm^{-1}.

pK_A Measurements.—A standard spectroscopic method[14] for determining pK_A values was used. Ultraviolet spectra were determined on solutions approximately 10^{-5} *M* in phenol or amine in 5% (w/w) methanol–water, using a 0–0.1-o.d. slide wire (Table II). The necessary pH determinations were made on a Radiometer pH meter, Model 4d, using a Type G-200B high pH electrode, on the 3-ml spectroscopic sample immediately after obtaining the ultraviolet spectrum. The analytical wavelength for the amine was 318 mμ, while for the phenol two wavelengths were used: 276 and 329.5 mμ.

TABLE II

ULTRAVIOLET SPECTRA

Compound	Solvent system	λ, mμ	Log ε
4-Hydroxy[2.2]paracyclophane	5% MeOH–H_2O[a]	224	4.172
		289	2.806
		310	2.748
4-Hydroxy[2.2]paracyclophane	95% EtOH[b]	224	4.17
		283	2.78
		290	2.87
		312	2.78
4-Hydroxy[2.2]paracyclophane, anion	5% MeOH–H_2O[a]	277	3.343
		329	1.136
4-Hydroxy[2.2]paracyclophane, anion	95% EtOH[b]	284	3.08
		332	2.75
4-Amino[2.2]paracyclophane,	5% MeOH–H_2O[a]	226	4.120
		270	3.314
		318	2.785
4-Amino[2.2]paracyclophane,	95% EtOH[b]	222	4.2
		272	3.41
		323	2.82
4-Amino[2.2]paracyclophane, cation	5% MeOH–H_2O[a]	223	4.238
		286	2.474
		307	2.143
4-Amino[2.2]paracyclophane, cation	95% EtOH[b]	223	4.26
		286	2.41
		303	2.13

[a] This work. [b] Reference 6.

From seven to nine different solutions were used for each determination. Typical Δo.d. values were 0.05 to 0.09. The pH meter was standardized against standard aqueous buffers between each reading. No correction was applied to meter readings for differences in the activity of acid or base in 5% methanol–water and water, since this correction would be small.[15] Solutions and cell compartments were at 25.0°. The pK_A of phenol, determined in this solvent, was 10.01 [lit.[16] (preferred values, 25°, in water, by eight investigators, using both potentiometric and spectroscopic methods) was 9.88 to 10.08].

Acknowledgment.—We are grateful to the Petroleum Research Fund of the American Chemical Society for support of this research under Grant 1475B.

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Test of the Reversibility of the Platinum-Catalyzed Hydrosilylation of Olefins

LEONARD SPIALTER AND DANIEL H. O'BRIEN[1]

Chemistry Research Laboratory,
Aerospace Research Laboratories, Office of Aerospace Research,
Wright-Patterson Air Force Base, Ohio

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The addition of silicon hydrides across unsaturated carbon–carbon bonds under the remarkably efficient catalysis by chloroplatinic acid and other platinum compounds has been extensively studied by Speier and co-workers,[2] as well as many others.[3] The tendency to form primary alkylsilanes from nonterminal olefins was observed,[2a,b,4] although other isomerizations have been noted.[5,6] The various recent mechanisms proposed[2b,4,7,8] have generally concurred that the terminal adduct observed does not arise from rearrangement of another adduct, but, instead, comes from isomerization of the olefin on the catalyst surface, either with or without the required presence of a hydrosilane, followed by the addition reaction.

The present report describes a test of whether or not there is a kinetically significant equilibrium involving the terminal addition compound and its precursors, the olefin, and the hydrosilane at temperatures up to 100° in the presence of homogeneous and heterogeneous platinum catalysts. For this purpose, an optically active alkyl substituent, (*S*)-2-methylbutyl, on silicon was selected since it contains only one asymmetric center, the β carbon, and this bears the requisite hydrogen atom. Moreover, suitable synthetic methods have already been developed for the necessary compounds.[9] If an equilibrium (eq 1) occurred with significant rate and physical separation of reactants, then racemization of the alkyl group should be observed.

$$\underset{\textbf{I}}{C_2H_5(CH_3)\text{–}C^*H\text{–}CH_2\text{–}SiX_3} \rightleftharpoons C_2H_5(CH_3)C{=}CH_2 + HSiX_3$$

$$\begin{array}{l} \text{a, } X = H \\ \text{b, } X = Cl \end{array} \qquad (1)$$

Under platinum-catalyzed hydrosilylation conditions (see Table I) attempts were made to racemize both (+)-(*S*)-2-methylbutylsilane (Ia) and (+)-(*S*)-2-methylbutyltrichlorosilane (Ib). The experimental results are given in Table II. The observed optical rotation values taken before and after each of the various runs show some shifts both negative and positive. However, these are considered to be within experimental

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[1] Visiting Research Associate under contractual arrangement with The Ohio State University Research Foundation.

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