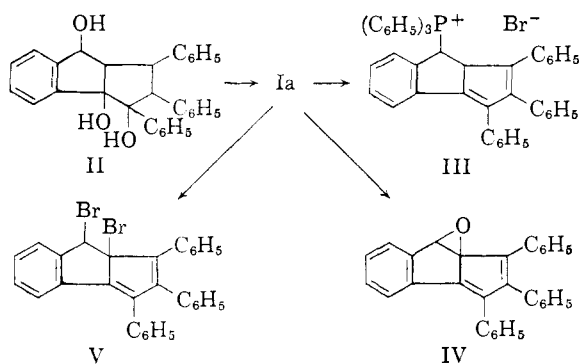110–120°. Calcd. for $C_{30}H_{24}O_3$: C, 83.31; H, 5.59; found: C, 83.31; H, 5.84. Infrared (chloroform): 2.82, 3.33, 5.85, 6.25μ] to the triol II [m.p. 241–242°. Calcd. for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03; found: C, 82.92; H, 6.04. Infrared (chloroform): 2.80, 2.92, 6.24μ]. Dehydration of triol II with phosphorus oxychloride in excess pyridine for 1 hr. at 80–90° afforded in 70% yield a green crystalline hydrocarbon, Ia [m.p. 186–187°. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380.5; found: C, 94.70, 94.50; H, 5.47, 5.47; mol. wt. 390 (Signer–Clark). $\lambda\lambda_{max}$ mμ (log ε): 272 (4.47), 293 (4.48), 409 (3.89), 425sh (3.85), 585 (2.39); $\lambda\lambda_{min}$ 240 (4.13), 278 (4.47), 351 (3.66), 500 (2.28), 791 (1.83) (cyclohexane). Infrared (chloroform): 3.24, 6.24, 6.34, 6.67, 6.73, 6.90 μ. N.m.r.(DCCl₃): complex benzenoid multiplet centered at τ = 3.1 and a singlet at τ = 3.75 (=CH—) in the ratio of 19:1. While Ia is stable to air, heat, and moderately strong acid (it is not extracted from a cyclo-

hexane solution with either 85% phosphoric or 50% sulfuric acids, but is slowly destroyed over several days), nucleophiles rapidly react with it. Strongly nucleophilic substances (pyrrolidine, hydroxide and methoxide ions) quickly destroy Ia while weaker nucleophiles rapidly form isolatable addition product: triphenylphosphine hydrobromide (in CH_3CN)[7] forms in 39% yield a yellow crystalline adduct, III [m.p. 189–190.5°. Calcd. for $C_{48}H_{36}BrP$: C, 79.66; H, 5.01; Br, 11.04; P, 4.28; found: C, 79.65; H, 5.24; Br, 11.00; P, 4.29. $\lambda\lambda_{max}$ mμ (log ε): 248 (4.51), 269 (4.43), 356 (4.03) (CH_3CN). N.m.r. (DCCl₃): doublet at τ = 1.27, complex benzenoid multiplet centered at τ = 2.6, and a doublet at τ = 4.17 in the approximate ratio of 1:34:1]. Alkaline hydrogen peroxide converts Ia in 71% yield to a light and air sensitive yellow compound [m.p. 166–167° (dec.). Calcd. for $C_{30}H_{20}O$: C, 90.88; H, 5.09; found: C, 90.11; H, 5.13. Infrared (chloroform): 3.34, 6.27, 6.37, 6.43μ. $\lambda\lambda_{max}$ mμ (log ε): 257 (3.35), 281 (4.35), 400 (3.68) (cyclohexane). N.m.r. (DCCl₃): complex benzenoid centered at τ = 2.8 and a singlet at τ = 5.15] tentatively assigned structure IV. Bromine in carbon tetrachloride instantly adds to Ia to form in 75% yield an orange dibromo adduct, V [m.p. 167–168°. Calcd. for $C_{30}H_{20}Br_2$: C, 66.67; H, 3.73; found: C, 66.77; H, 3.98. $\lambda\lambda_{max}$ mμ (log ε): 253 (4.45), 293 (4.38), 393 (3.59) (cyclohexane). N.m.r. (DCCl₃): complex benzenoid multiplet centered at τ = 2.8 and

(7) H. Hoffman, *Ber.*, **94**, 1331 (1961).

a singlet at τ = 3.53]. Alkaline permanganate oxidation of Ia affords benzil and benzoic acid.

To establish unambiguously the trisubstituted benzopentalene structure for Ia the methoxy labeled derivative, Ib [m.p. 176–177°. Calcd. for $C_{31}H_{22}O$: C, 90.70; H, 5.40; found: C, 90.53; H, 5.62. $\lambda\lambda_{max}$ mμ (log ε): 225sh (4.42), 268 (4.54), 303 (4.54), 391sh (3.88), 408 (3.91), 605 (2.59). N.m.r. (DCCl₃): complex benzenoid multiplet centered at τ = 3.1, a singlet at τ = 3.72 (=CH—), and methoxy singlet at τ = 6.28] was prepared in a manner analogous to Ia and oxidized with alkaline permanganate. The identification of benzil and p-methoxybenzoic acid among the oxidation products coupled with the observed physical and chemical properties are only compatible with a triarylated benzopentalene.
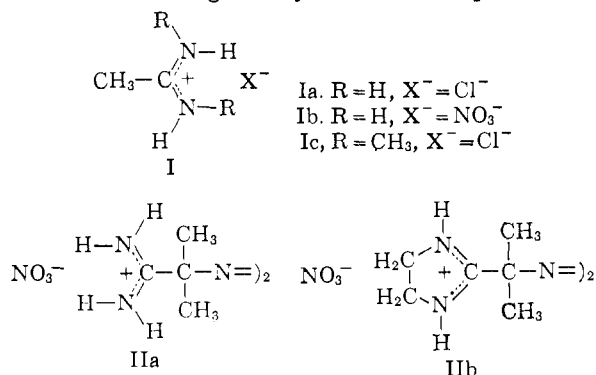
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THE NATURE OF AMIDINIUM GROUPS

Sir:

Structures of amidinium salts of types I and II have been investigated by n.m.r. techniques.

Ia. R = H, X⁻ = Cl⁻
Ib. R = H, X⁻ = NO₃⁻
Ic, R = CH₃, X⁻ = Cl⁻

I

IIa   IIb

These conclusions have been reached: (1) rotation about C⋯N bonds is restricted; (2) compound Ic exists in the configuration indicated with magnetically nonequivalent pairs of H's and R's and *nitrogens which differ in chemical reactivity;* (3) proton exchange in dilute aqueous acid involves hydroxide ion and (4) exchange in strongly acidic media involves formation of second conjugate acids.

The spectra of Ia–c and IIa in anhydrous dimethylsulfoxide (Table I) show two resonance signals of equal intensity for nitrogen protons.

TABLE I
CHEMICAL SHIFTS OF GROUPS ATTACHED TO NITROGEN IN AMIDINIUM SALTS

Compound	Solvent	N–H(c.p.s.)[a]	N–CH₃(c.p.s.)[a]
Ia	DMSO[b]	530, 560	....
Ib	DMSO	530, 560	....
Ic	DMSO	554, 609	171.5, 176.5[c]
Ic	H₂O	.....	177.5, 187.0
Ic	15% H₂SO₄–H₂O	~425, ~455	179.0, 188.5[c]
IIa	DMSO	534, 547	....
IIb	DMSO	608	....

[a] Referred to tetramethylsilane (external), downfield, 60 M., room temperature. [b] Dimethylsulfoxide. [c] Positions of doublet centers (J = 5.0 c.p.s. for each doublet).

The formulas of the compounds indicate that there should be distinguishable "inside" and "outside" proton sites. As is observed, Ic should show two N–CH₃ resonances in the indicated configuration. The alternative hypothesis that Ic exists as a mixture of species can be rejected.[1] Steric arguments indicate that the unsymmetrical configuration is less strained than the alternate, symmetrical, structures.

The N—CH₃ resonance of Ic in H_2O–H_2SO_4 mixtures varies markedly. In water there are two, unsplit peaks. In solutions 15–60 weight per cent. in sulfuric acid the two peaks are split into doublets. This splitting is due to adjacent N–H protons as is shown by the disappearance of the doublet structure when protons are replaced by deuterons. As the concentration of acid is further increased the doublets collapse; only two broad singlets appear in 85% sulfuric acid. Above 85% sulfuric acid the singlets coalesce and a single N–CH₃ resonance is observed in "concentrated" sulfuric acid. The following scheme provides an interpretation of the data: (1) in water solution coupling between N–H and N–CH₃ protons is destroyed by rapid exchange of N–H protons with solvent; however, such exchange does not permit free rotation about C⋯N bonds; (2) at intermediate acidities the residence time of protons attached to nitrogen is long enough to allow observable spin coupling; (3) in media of high acidity proton exchange, involving formation of a second conjugate acid, again decreases the residence time of N–H protons in unique spin states; (4) finally, lifetimes of second conjugate acids become long enough to cause magnetic equivalence of N–CH₃ groups by rotation about C–⁺NH₂CH₃ bonds.

Collapse of the two N–CH₃ doublets at intermediate concentrations of sulfuric acid is *non-simultaneous*. *The high field doublet collapses at lower acidities than the low field doublet*, indicating that the basicities of the two nitrogen atoms are different.

Collapse of the N–H doublet of Ia in DMSO has been studied over the temperature range 30–115°. An activation energy[2] of 7 ± 2 kcal./mole and frequency factor of 10^3–10^7 have been calculated. The similarity of these parameters to those characteristic of the collapse of the N–CH₃ doublet of N,N-dimethylformamide[3] is consistent with the view that the interconversion is accomplished by rotation about C=N bonds. Measurement of transverse relaxation times for the water resonance in dilute aqueous acid solutions of Ia shows that the mean lifetime of protons on a water molecule is directly proportional to $[H^+][H_2O]/[Ic]$. Of all mechanisms for exchange in dilute acid solution considered by Grunwald, *et al.*,[4]

only the one involving hydroxide-catalyzed exchange fits this law. A reasonable value of 8×10^{10} sec.$^{-1}$ is estimated for the rate constant at 33°. Collapse of the two N–CH₃ resonances of Ic in concentrated acid was studied in concentrated D_2SO_4; $1/\tau$ is a linear function of d_0 in the D_0 interval -7.50 to -8.00, showing that protonation is responsible for exchange of the environments of the methyl groups. The rates of collapse of the two N–CH₃ doublets have been estimated in 28.4% D_2SO_4. The high field doublet was almost completely collapsed approximately 15 seconds after mixing whereas the low field doublet was almost intact. Collapse of the latter was complete within about three minutes. This observation provides a direct comparison of the rates of proton exchange at the two nitrogen atoms.

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A NON-AROMATIC ROUTE TO A PARACYCLOPHANE[1]

Sir:

The strained[2] macrocyclic species [2.2]paracyclophane (III) has been prepared by three routes, each utilizing a suitable aromatic precursor. As a minor product in the pyrolysis of *p*-xylene,[3] III is isolated in *ca.* 0.3% yield employing a fast flow technique at 1065°.[4] Compound III also can be prepared (2%) by the intramolecular Wurtz-coupling[5] of 4,4′-bis-(bromomethyl)-bibenzyl, but most conveniently and in high yield (17%) by a 1,6-Hofmann elimination[6] on pyrolysis of *p*-methylbenzyltrimethylammonium hydroxide (I, A = NMe₃OH). The two pyrolytic syntheses utilize the formation of the very reactive intermediate *p*-xylylene (II).[7]

I   II   III
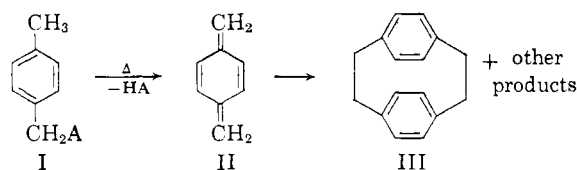
An alternative "non-aromatic" route to a *p*-xylylene and subsequently a paracyclophane can be envisioned. A four-fold elimination reaction on a judiciously chosen cyclohexane derivative would yield a tetraolefin with the requisite degree of

(1) The spectra could also be accounted for if the symmetrical structures were present in equal amounts, and the resonances of inside and outside N–H and N–CH₃ groups were independent of the configuration of the second nitrogen atom; an unlikely possibility.

(2) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959, p. 218.

(3) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); H. S. Gutowsky, D. W. McCall and C. P. Slichter, *ibid.*, **21**, 279 (1953); W. D. Phillips, *ibid.*, **23**, 1363 (1955).

(4) E. Grunwald, A. Lowenstein and S. Meiboom, *ibid.*, **27**, 630 (1957).

(1) Research supported by the U. S. Army Research Office (Durham).

(2) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

(3) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(4) L. A. Errede and J. P. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960).

(5) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).

(6) H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

(7) The chemistry of *p*-xylylene has been reviewed recently: L. A. Errede and M. Szwarc, *Quart. Revs. (London)*, **12**, 301 (1958).