55° for 4 hr. gave (besides other products) *ca.* 5% of the cyclic "trimer", cyclotriaconta-1,3,7,11,13,17,21,23,27-nonayne (III) [m.p. 198–199° dec.; $\lambda_{\max}^{\text{isoöctane}}$ 226,234 and 255 mμ; found: C, 93.68; H, 6.27]; full hydrogenation (platinum, dioxane) yielded cyclotriacontane, m.p. and mixed m.p. 56–57°.

Rearrangement of III with potassium *t*-butoxide in *t*-butyl alcohol–benzene[1,3] at 90° for 20 minutes led to *ca.* 20% of an isomer, dark brown-violet crystals from pentane-ether (red in solution), which decomposed when heated; $\lambda_{\max}^{\text{dioxane}}$ 320 and 401 mμ (ϵ = 51,000 and 113,000); $\lambda_{\max}^{\text{benzene}}$ 323 and 406 mμ (ϵ = 47,000 and 108,000). The infrared spectrum (KBr) showed bands at 3.31 μ (—CH=), 4.64 μ (—C≡C—), 7.09 μ (*cis*-double bond), 7.76 and 10.33 μ (*trans*-double bond). Full hydrogenation (platinum, dioxane) gave cyclotriacontane, m.p. and mixed m.p. 57–58°. The rearrangement product is clearly a fully conjugated dodecaene-triyne and a symmetrical 1,11,21-triyne structure (IV or a stereoisomer) appears most probable.

Both the fully conjugated systems described are reasonably stable and can be kept with little change in light and air for 24 hr. in the solid state or for several weeks in dilute benzene solution.

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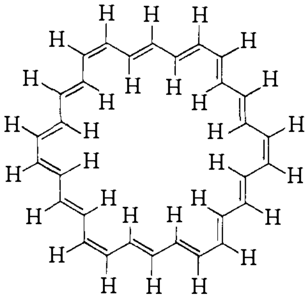
RECEIVED DECEMBER 19, 1959

UNSATURATED MACROCYCLIC COMPOUNDS. XIII.[1] CYCLOTRIACONTAPENTADECAENE

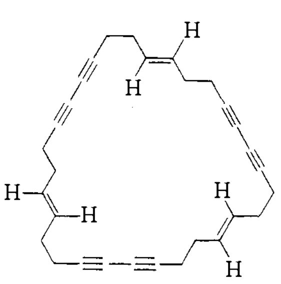
Sir:

Cyclotriacontapentadecaene (CTP) (I) is a fully conjugated cyclic polyene which was expected to exhibit aromatic character, since it contains ($4n + 2$) π-electrons ($n = 7$) and it probably can exist in a planar configuration. In fact CTP has been postulated as the smallest conjugated cyclic polyene with aromatic properties,[2] as the degree of proximity which exists between *every* "internal" hydrogen atom in cycloöctadecanonaene[3] exists only between every *alternate* "internal" hydrogen atom in CTP. We now describe two syntheses of CTP and experiments which indicate that in fact this does not represent a stable system.

Cyclotriacontadecaenepentayne (formula II or stereoisomer in the preceding Communication)[1] in benzene was allowed to absorb 5 moles of hydrogen over a "Lindlar" palladium catalyst. Chromatography on alumina first gave starting material and then *ca.* 5% of a substance, dark brown-red crystals from ether, which decomposed on heating; $\lambda_{\max}^{\text{dioxane}}$ 329 and 428 mμ (ϵ = 44,000 and 144,000); $\lambda_{\max}^{\text{benzene}}$ 331 and 432 mμ (ϵ = 43,000 and 140,000). The infrared spectrum (KBr) no longer showed the acetylene band at 4.64 μ. Although the new compound was too unstable for accurate elemental analysis, the results obtained with two different samples (found: C, 88.82, 88.52; H, 7.36, 7.52) indicated a $C_{30}H_{30}$ formula (C:H ratio = 30:29.6; 30:30.4). Full hydrogenation (platinum. dioxane) gave cyclotriacontane, m.p. and mixed m.p. 56–57°.



I



III

$H\text{-}(-C{\equiv}CCH_2CH_2CH\overset{t}{=}CHCH_2CH_2C{\equiv}C-)_n\text{-}H$

IIa, $n = 1$
b, $n = 2$

The data show the partial hydrogenation product to be a CTP. Although it is not known with certainty whether it is the 1,11,21-tri-(*cis*)-ene (I) or a stereoisomer, evidence for structure I is provided by the fact that the same substance is obtained (as indicated by the identical ultraviolet spectrum and chromatographic behavior) in *ca.* 10% yield through the addition of 3 moles of hydrogen to cyclotriacontadodecaenetriyne (formula IV or stereoisomer in the preceding Communication)[1] in benzene over a Lindlar catalyst.

The synthetic CTP is unstable, being destroyed by standing in light and air for several hours or attempted isomerization with a trace of iodine in boiling benzene; it also gradually decomposes in dilute benzene or dioxane solution at room temperature.

Although the possibility exists that the instability of the synthetic CTP is due to it being a stereoisomer of I which is not planar, the series of experiments reported provides independent evidence that I is not an aromatic system.

Reaction of *trans*-1,4-dibromo-2-butene with allenylmagnesium bromide (from propargyl bromide, magnesium and mercuric chloride)[4] catalyzed with cuprous chloride gave *ca.* 50% of *trans*-5-decene-1,9-diyne (IIa) [b.p. 81–82° (20 mm.), $n^{19}D$ 1.4701; found: C, 90.55; H, 9.12; act. H, 1.50]. Oxidation with cupric acetate in pyridine at 65° for 3.5 hr. yielded (besides other products) *ca.* 2.5% of the cyclic trimer, cyclotriaconta-1,11,21-tri-(*trans*)-ene-5,7,15,17,25,27-hexayne (III) (m.p. 111–112°; $\lambda_{\max}^{\text{isooctane}}$ 226, 240 and 254 mμ; found: C, 91.59; H, 7.54). Full hydrogenation (platinum, dioxane) led to cyclotriacontane, m.p. and mixed m.p. 57–58°.

Attempted isomerization of III with potassium *t*-butoxide in *t*-butyl alcohol–benzene at 90°, then careful chromatography on alumina, gave no indication that a conjugated CTP of type I had been formed in reasonable yield. On the other hand, the same conditions resulted in the isomerization of the monomer IIa to 1,3,5,7,9-decapentaene (15% yield; m.p. 145–147° dec.; $\lambda_{\max}^{\text{isooctane}}$ 291, 303, 317 and 334 mμ)[5] and of the linear dimer IIb (m.p. 57°) to

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(1) Part XII, see F. Sondheimer, R. Wolovsky and Y. Gaoni, THIS JOURNAL, **82**, 754 (1960).

(2) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

(3) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, No. 3, 3 (1959).

(4) See M. Gaudemar, *Ann. chim. (Paris)*, (1) **13**, 190 (1956) C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar and M. Andrac, *Bull. soc. chim. France*, 679 (1959).

(5) A. D. Mebane, THIS JOURNAL, **74**, 5227 (1952).

1,3,5,7,9,11,13,15,17,19-eicosadecaene [$\lambda_{\max}^{\text{isooctane}}$ (principal bands) 376, 397, 420 and 447 mμ].[6]

[6] F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, to be published.

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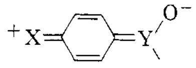
RECEIVED DECEMBER 19, 1959

SOLVENT EFFECTS ON MESOMERIC CHARGE SEPARATION[1]

Sir:

Reactivity[2] and dipole moment[3] data have suggested that the contribution to the resonance hybrid of dipolar resonance structures, *e.g.*



is enhanced by solvents which support ionization.

We report herein unequivocal evidence for such phenomena based upon the difference in the F^{19} n.m.r. shielding parameters for substituents in the *p*- and *m*-positions of fluorobenzene, $\mathcal{S}_p^F - \mathcal{S}_m^F$. This quantity (hereafter referred to as the mesomeric charge perturbation, m.c.p.) provides a quantitative measure of the order of electron densities in the immediate vicinity of the F^{19} nucleus produced by mesomeric interaction of the *para* substituent.[2c,4]

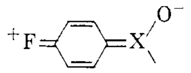
TABLE I

MESOMERIC CHARGE PERTURBATIONS (M.C.P.'S), $\mathcal{S}_p^F - \mathcal{S}_m^F = H_m^F - H_p^F$ (IN P.P.M.), FOR SUBSTITUTED FLUOROBENZENES

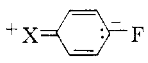
Subst.	Class	Solvent Cyclo-C_6H_{12}	CCl_4	CH_3OH	75% aq. CH_3OH	Av.
NH_2	−R	−13.8 ± 0.1	−13.8 ± 0.2	−13.4 ± 0.1	−12.9 ± 0.1	...
OCH_3	−R	−12.6 ± 0.1	−12.6 ± 0.1	−12.6 ± 0.2	−12.5 ± 0.1	−12.6
OH	−R	−12.1 ± 0.1	−12.2 ± 0.1	−13.5 ± 0.2	−13.0 ± 0.2	...
F	−R	− 9.8 ± 0.1	− 9.8 ± 0.3	− 9.7 ± 0.1	− 9.5 ± 0.0	− 9.7
$OCOCH_3$	−R	− 6.0 ± 0.1	− 6.0 ± 0.1	− 5.8 ± 0.1	− 5.7 ± 0.1	− 5.9
Cl	−R	− 5.1 ± 0.1	− 5.1 ± 0.1	− 5.1 ± 0.1	− 4.9 ± 0.1	− 5.1
CO_2H	+R	(insol.)	(insol.)	6.4 ± 0.1	6.6 ± 0.1	...
$CO_2C_2H_5$	+R	5.8 ± 0.1	6.1 ± 0.1	6.5 ± 0.1	6.6 ± 0.1	...
CH_3CO	+R	5.6 ± 0.1	5.9 ± 0.1	6.6 ± 0.1	7.3 ± 0.1	...
NO_2	+R	5.8 + 0.1	5.8 ± 0.1	6.5 ± 0.1	7.2 ± 0.1	...
CHO	+R	7.8 ± 0.1	8.1 ± 0.2	...	9.0 ± 0.1	...

Table I records m.c.p.'s for a variety of typical −R and +R substituents in four solvents at "infinite dilution." The m.c.p. values for most −R substituents show a second order dependence on solvent which cannot with confidence be taken to appreciably exceed the limits of the present experimental error. Apparently the average m.c.p.'s listed for these substituents are therefore approximate intramolecular properties. The only exceptions to this behavior are the two −R substituents, OH and NH_2, for which the m.c.p. can be influenced by hydrogen bonding between the substituent and the hydroxylic solvents. Consistent with such an interpretation are the facts that the m.c.p. values for the proton donating OH group are more negative (greater electron density) and those for the proton accepting NH_2 group are less negative in hydroxylic than in the non-hydroxylic solvents.

In contrast, the m.c.p.'s for *every* +R substituent show that the electron density at the F^{19} atom is decreased appreciably with increased ability of the solvent to support ionization. The nature of the present results is such that these solvent effects must be ascribed to the increased contribution to the resonance hybrid of the dipolar resonance form[5]



It is of interest to note in connection with the nearly solvent independent character of the m.c.p.'s for the −R substituents that the contribution to the resonance hybrid of the dipolar canonical form



is apparently much less dependent upon solvent than that of the above type.[2c]

Solutions 5% (by vol.) in the substituted fluorobenzene were employed and the shifts obtained[2c] relative to the internal standard (2%) tetrafluorotetrachlorocyclobutane.[6] We are much indebted to Dr. G. V. D. Tiers for suggesting and supplying a sample of this standard.

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[1] This work was supported in part by the Office of Naval Research, Project NR055-328.

[2] (a) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 559 (1953); (b) M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bur. Stand.*, **60**, 569 (1958); (c) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis and R. E. Glick, THIS JOURNAL, **81**, 5352 (1959).

[3] J. W. Smith, *J. Chem. Soc.*, 109 (1953).

[4] H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

[5] R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

[6] G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

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RECEIVED NOVEMBER 23, 1959