is 37.6 kcal./mole. This represents the highest value we have yet encountered for the heat of hydrogenation of an ethylenic linkage (cyclohexene, -27.1 kcal./mole[2]; cis-di-t-butylethylene, -36.2 kcal./mole[3]). The incorporation of a high degree of strain in the barrelene molecule is evident from examination of Dreiding models.

Although the present result does not rigorously exclude the possibility of ground-state delocalization in barrelene, it is clear that such stabilization, if present, is swamped by steric strain.

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged.

(3) R. B. Turner, D. E. Nettleton, and M. Perelman, J. Am. Chem. Soc., **80**, 1430 (1958).

DEPARTMENT OF CHEMISTRY   RICHARD B. TURNER
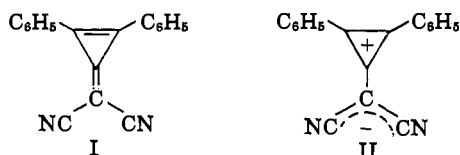RICE UNIVERSITY
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1-Dicyanomethylene-2,3-diphenylcyclopropene ("1,1-Dicyano-3,4-diphenyltriafulvene")[1]

Sir:

Among the nonalternant pseudoaromatic systems that of methylenecyclopropene[2] ("triafulvene")[3] was unknown until recently, when three compounds of this type have been described.[4-6] We wish to report another representative of this group, 1-dicyanomethylene-2,3-diphenylcyclopropene, in which both the classical (I) and the dipolar (II) structure make a contribution to the ground state of the molecule. We ex-

pected the dipolar form of the triafulvene, in which the negative charge is localized mostly at the exocyclic carbon atom (C-1), to be enhanced by such electronegative substituents as the nitrile group.

Refluxing diphenylcyclopropenone[7] and malononitrile in freshly distilled acetic anhydride and recrystallization from benzene gave a 4.8% yield of yellowish crystals, m.p. 294° dec. *Anal.* Calcd. for $C_{18}H_{10}N_2$: C, 85.0; H, 4.0; N, 11.0; mol. wt., 254. Found: C, 85.2; H, 4.2; N, 10.8; mol. wt., 254 (by mass spectroscopy).[8,9] The infrared spectrum of the compound (in Nujol) showed strong peaks at 2227, 1890, 1618, 1522, 1488, 1466, 1397, 777, and 693 cm.$^{-1}$, the most

(1) Fulvenes and Thermochromic Ethylenes, part 34. Part 33: E. D. Bergmann and R. Ikan, J. Org. Chem., **28**, 3341 (1963).

(2) Cf. E. D. Bergmann, "The Fulvenes," in "Progress in Organic Chemistry," Vol. 3, 1955, p. 81.

(3) "Triangle" is the trivial name recently suggested by O. Chalvet, R. Daudel, and J. J. Kaufman, J. Phys. Chem., **68**, 490 (1964).

(4) A. S. Kende, J. Am. Chem. Soc., **85**, 1882 (1963).

(5) M. A. Battiste, ibid., **86**, 942 (1964).

(6) W. M. Jones and J. M. Denham, ibid., **86**, 944 (1964).

(7) R. Breslow, J. Posner, and A. Krebs, ibid., **85**, 234 (1963). We are grateful to Professor R. Breslow for a detailed descripion of the preparation of this ketone.

(8) The analogous heptafulvene derivative has been prepared by the same method by Y. Kitahara and K. Doi [Japanese Patent 13071; Chem. Abstr., **59**, 9914 (1963)].

(9) We are indebted for the mass-spectroscopic investigation of the compound to Dr. Z. Pelah at the Chemistry Department, Stanford University, Stanford, Calif.

interesting among them being the one at 1890 cm.$^{-1}$. It appears in the three other methylenecyclopropene derivatives known[4-6] at 1828, 1835, and 1852 cm.$^{-1}$, respectively, and represents, in our opinion, the shifted frequency (1818 cm.$^{-1}$) of the cyclic double bond observed in 1,2-diphenylcycloprop-1-ene derivatives.[10] This would tend to show that the classical form I makes a significant contribution to the ground state of the molecule.

The n.m.r. spectrum in anhydrous trifluoroacetic acid[11] showed two unresolved multiplets at τ 1.95 and 2.32 (tetramethylsilane as standard) with relative areas 2:3. As we found for diphenylcyclopropenone in trifluoroacetic acid (τ 2.05 and 2.37) and $CDCl_3$ (τ 2.20 and 2.55) the same ratio of areas (2:3), we assume that the two signals correspond to the *ortho-* and the *meta- plus para-*hydrogen atoms of the phenyl rings.[12]

It is noteworthy that C-1 of I is not protonated under these circumstances as only the above multiplets have been found.

The ultraviolet spectrum was measured in dioxane (longest band: 363 mμ (log ϵ 4.00)), acetonitrile (352 (4.07)), trifluoroacetic acid (335 (4.23)), and mesitylene (373 (3.91)). The dependence of the wave length on the solvent seems to indicate that in the excited state the "fulvenic" (dipolar) form of the molecule (II) makes a significant contribution; of interest is the considerable shift observed in concentrated sulfuric acid: 386 mμ (log ϵ 3.64). This may be due to a *chemical* reaction of the solvent with the solute. This hypothesis is supported by the observation that heating of I with 90% sulfuric acid at 100° (15 min.) gives a product (from acetic acid, m.p. 199–200° (dec.)) which, according to the analysis, is the corresponding diamide *plus* one molecule of H_2SO_4. *Anal.* Calcd. for $C_{18}H_{16}N_2O_6S$: C, 55.7; H, 4.2; N, 7.2; S, 8.2. Found: C, 55.9; H, 4.1; N, 7.0; S, 7.8.

Finally, we wish to report the dipole moment 7.9 $\pm$ 0.1 D. of I (in dioxane at 30°). This figure points to the contribution of the dipolar form (II) to the ground state of the molecule as shown by comparison with the moments of cyclohexylidenemalononitrile (5.45 $\pm$ 0.02 D. in benzene at 30°), diphenylmethylenemalononitrile (5.85 $\pm$ 0.05 D. in benzene at 30°), ω,ω-dicyanodibenzofulvene (5.53 $\pm$ 0.07 D. in benzene at 30°), and ω,ω-dicyanoheptafulvene (7.49 D. in dioxane at 25°).[13] Thus, 1,1-dicyano-3,4-diphenyltriafulvene in its ground state is a resonance hybrid of I and II.

(10) See, e.g., R. Breslow, J. Lockhart, and H. W. Chang, J. Am. Chem. Soc., **83**, 2375 (1961); R. Breslow and H. W. Chang, ibid., **83**, 2367 (1961).

(11) The substance proved insoluble in deuteriochloroform.

(12) For this explanation, cf. R. Breslow, H. Höver, and H. W. Chang, J. Am. Chem. Soc., **84**, 3168 (1962).

(13) This value was reported by M. Yamakawa, et al., ibid., **82**, 5665 (1960).

DEPARTMENT OF ORGANIC CHEMISTRY   ERNST D. BERGMANN
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An Aliphatic Triafulvene[1]

Sir:

The synthesis of the crystalline quinocyclopropene I,[2] the first stable derivative of the triafulvene system,

(1) "Triafulvene" is the concise trivial name suggested by E. D. Bergmann and I. Agranat for the methylenecyclopropene system.
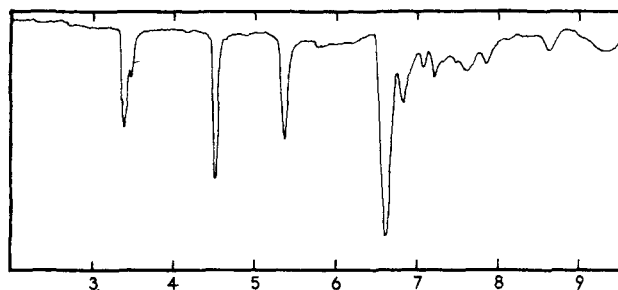
(2) A. S. Kende, J. Am. Chem. Soc., **85**, 1882 (1963).

Fig. 1.—Infrared spectrum of triafulvene III in CCl₄ solution; principal maxima are at 4.51 (CN), 5.32 (C=C), and 6.61 μ.

has been followed by the preparation of three other triafulvenes represented by structures IIa (R_1 = H, R_2 = $COOC_2H_5$),[3] IIb (R_1 = $COOCH_3$, R_2 = CH_2-$COOCH_3$),[4] and IIc (R_1 = R_2 = CN).[5] There is little doubt that each of these highly strained molecules receives extra stabilization from the electron-withdrawing exocyclic substituents which produce appreciable cyclopropenium character in the alicyclic ring.[6] On the other hand, it is not clear whether the two phenyl substituents on the ring play a stabilizing role, and certainly their presence obscures the spectroscopic and chemical properties of the theoretically interesting methylenecyclopropene system. We therefore describe the following facile synthesis of the first fully aliphatic triafulvene, III.

III
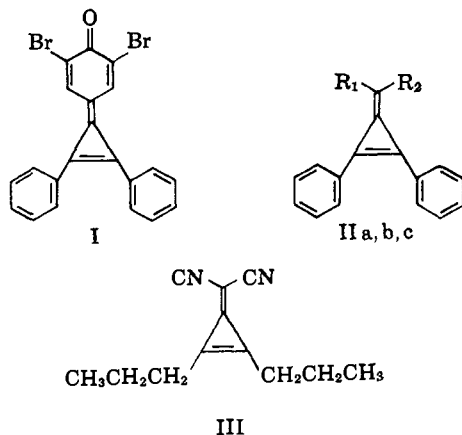
Treatment of 2.5 g. of di-n-propylcyclopropenone with 1.25 g. of malononitrile in 30 ml. of acetic anhydride at 140° for 2 hr. under a nitrogen atmosphere converted the ketone into a mixture of products, as indicated by infrared maxima (after removal of acetic anhydride) at 5.32, 5.51, and 5.76 μ (CCl₄ solution). Short-path distillation at 62-78° (0.2 mm.) removed the fractions responsible for the two higher bands and continued distillation at 110-115° (0.1 mm.) produced a straw-colored liquid (18% yield) which exhibited the strikingly simple infrared spectrum (Fig. 1) expected for the symmetrical triafulvene III. This structure was further confirmed by combustion data

(3) M. A. Battiste, J. Am. Chem. Soc., 86, 942 (1964).

(4) W. M. Jones and J. M. Denham, ibid., 86, 944 (1964).

(5) E. D. Bergmann and I. Agranat, ibid., 86, 3587 (1964). We are indebted to these authors for communicating their data to us prior to publication.

(6) Compare, for example, the stability of 8,8-dicyanoheptafulvene [T. Nozoe, T. Mukai, K. Osaka, and N. Shishido, Bull. Chem. Soc. Japan, 34, 1384 (1961)] with that of the very unstable parent. heptafulvene [W. von E. Doering and D. W. Wiley, Tetrahedron, 11, 183 (1960)].

(Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 76.77; H, 7.42; N, 15.01), mass spectrum (parent peak m/e = 186), and by the 60 Mc. proton magnetic resonance spectrum which showed only a unique propyl group. The resonance positions of the methylene α and β to the ring appear at τ 7.13 and 8.14, respectively, in CDCl₃ solution. Addition of 20 vol. % trifluoroacetic acid to the CDCl₃ solution had no effect on the resonance spectrum in the region τ 0 to 10, consistent with the observation by Bergmann and Agranat[5] that the triafulvene IIc remains unprotonated under similar conditions. The negligible basicity of III is paralleled by its failure to react with bromine in methylene chloride at room temperature[7] and by its inertness to tetracyanoethylene in cold acetonitrile.[8]

The proton chemical shift of a methyl group directly attached to cationoid carbon has been employed as a probe of the π-electron density on the cationoid center.[9] Alternatively, the internal chemical shift between the α- and β-methylenes of a propyl chain attached to an electron-withdrawing group has been used as a rough measure of group electronegativity.[10] Table I lists

TABLE I

Model	Solvent	$\tau_{\alpha\text{-}CH_2}$	$\tau_{\beta\text{-}CH_2}$	q_π
H triangle, $CH_3CH_2CH_2$ / $CH_2CH_2CH_2$ (α β)	CF_3CO_2H[10b]	6.72	7.99	ca. +0.33
$CH_2CH_2CH_3$ triangle, $CH_3CH_2CH_2$ / $CH_2CH_2CH_3$ (α β)	50% H_2SO_4	6.58[a]	7.88[a]	+0.33
COOCH₃ H triangle, $CH_3CH_2CH_2$ / $CH_2CH_2CH_3$ (α β)	CHCl₃	7.62	8.40	0
NC CN triangle, $CH_3CH_2CH_2$ / $CH_2CH_2CH_3$ (α β)	CHCl₃	7.13	8.14	Calcd. +0.16[b]
	CF_3CO_2H	7.16	8.15	+0.14[c]

[a] τ-Values given are extrapolated to CF_3CO_2H solvent by addition of 0.97 p.p.m. to the resonances reported in ref. 10b. [b] Net π-electron density on each propyl-bearing ring carbon interpolated from the chemical shift of the α-methylene. [c] Net π-electron density on each propyl-bearing ring carbon interpolated from the internal chemical shift between α- and β-methylenes.

the relevant parameters for three model compounds and for the triafulvene III. To the extent that these values reflect charge density on the ring carbon rather than a ring-current effect, both methods indicate a net charge of ca. +0.15 for the propyl-bearing ring carbons in III.[11]

(7) In contrast we find that the methyl ester of 2,3-dipropyl-2-cyclopropene-1-carboxylic acid rapidly decolorizes bromine in CH₂Cl₂.

(8) The triafulvene IIa is reported[3] to react "immediately" with tetracyanoethylene under these conditions.

(9) (a) C. MacLean and E. L. Mackor, Mol. Phys., 4, 241 (1961); (b) T. J. Katz and E. H. Gold, J. Am. Chem. Soc., 86, 1600 (1964).

(10) (a) J. R. Cavanaugh and B. P. Dailey, J. Chem. Phys., 34, 1099 (1961); (b) R. Breslow, H. Hover, and H. W. Chang, J. Am. Chem. Soc., 84, 3168 (1962).

(11) A linear relation between electron density and chemical shift within this series is assumed, as, for example, in ref. 9b. This assumption gives for the present case a proportionality constant for $\tau_{\alpha-CH_2}$ of 2.94 p.p.m. per unit charge, as compared with 3.27 p.p.m. per unit charge in ref. 9b.

Finally, the ultraviolet spectrum of the triafulvene III in cyclohexane shows an essentially symmetric single maximum at 246 mμ (log ϵ 4.30); in methanol the maximum is at 245 mμ (log ϵ 4.33). There is evidence neither for absorption above 300 mμ nor for a solvent effect as is found for other triafulvenes, and the position of the maximum suggests qualitative agreement with Julg's prediction[12] that the longest wave length (V $\leftarrow$ N) absorption for methylenecyclopropene will fall near 200 mμ.

(12) A. Julg, J. chim. phys., 50, 652 (1953).

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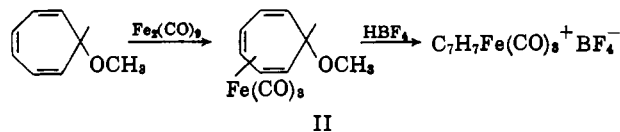
RECEIVED JULY 15, 1964

The Tropylium–Iron Tricarbonyl Cation

Sir:

Organometallic cationic complexes of the type LM(CO)$_3^+$ in which L is a tropylium ring π-bonded to a metal (M) are known for the group VI-B metals chromium,[1] molybdenum,[2] and tungsten.[3] The presumed structure of these complexes is indicated in formula I. The seven carbon atoms of the ring are symmetrically bonded to the metal by means of the six π-electrons, and the metal attains the effective atomic number of the next inert gas.[4]

I
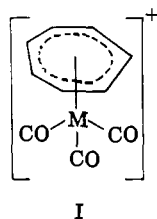
The analogous cationic complex containing iron is of some theoretical interest for, if the bonding in such a complex were to be similar, the effective atomic number of iron would exceed that of krypton by two.

Previous attempts to prepare salts of the tropylium–iron tricarbonyl cation have been unsuccessful.[5] Whereas the triphenylmethyl cation abstracts hydride ion from cycloheptatriene–M(CO)$_3$ complexes (M = Cr, Mo, and W) to give tropylium–M(CO)$_3$ complexes, in the case of cycloheptatriene–iron tricarbonyl addition occurs to give a substituted cycloheptadienyl–iron tricarbonyl cation.[6]

We now wish to report the synthesis of the tropylium–tricarbonyl cation by the following route.

II

(1) J. D. Munro and P. L. Pauson, J. Chem. Soc., 3475 (1961).
(2) H. J. Dauben, Jr., and L. R. Honnen, J. Am. Chem. Soc., 80, 5570 (1958).
(3) H. J. Dauben, Jr., L. R. Honnen and D. J. Bertelli, Abstracts, 15th Southwest Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 3, 1959, p. 89.
(4) D. A. Brown, J. Inorg. Nucl. Chem., 10, 39 (1959).
(5) An account of these is given in ref. 6.
(6) H. J. Dauben, Jr., and D. J. Bertelli, J. Am. Chem. Soc., 83, 497 (1961).

Treatment of methyl tropyl ether with iron enneacarbonyl gave the corresponding iron tricarbonyl complex (II) which reacted with fluoroboric acid to give the fluoroborate salt of the tropylium–iron tricarbonyl cation. The salt crystallizes in yellow needles from nitromethane, m.p. 112° dec. (Anal. Calcd. for C$_7$H$_7$-Fe(CO)$_3$BF$_4$: C, 37.78; H, 2.22; B, 3.18. Found: C, 37.44; 2.03; B, 3.32). It is stable in inert atmosphere but hydrolyzes rapidly in water to give tropyl alcohol–iron tricarbonyl from which the cation can be regenerated by treatment with fluoroboric acid.

As with the chromium, molybdenum, and tungsten complexes, the n.m.r. spectrum of the tropylium–iron tricarbonyl cation shows a single sharp absorption, but further comparison of these complexes reveals several significant differences. The pK_{R^+} values listed in Table I indicate that the tropylium–iron tricarbonyl cation is slightly less stable than the tropylium cation, whereas the group VI-B metal complex cations are considerably more stable.

TABLE I

Complex	τ^a	p$K_{R^+}{}^b$
C$_7$H$_7^+$BF$_4^-$	0.72	4.7
C$_7$H$_7^+$Fe(CO)$_3$BF$_4^-$	4.20	4.5
C$_7$H$_9^+$Fe(CO)$_3$BF$_4^-$	...	4.7
C$_7$H$_7^+$Cr(CO)$_3$BF$_4^-$	3.42	6.3
C$_7$H$_7^+$Mo(CO)$_3$BF$_4^-$	3.82	6.2
C$_7$H$_7^+$W(CO)$_3$BF$_4^-$	3.83	~6^c

^{a} Position of single n.m.r. peak measured in liquid SO$_2$. ^{b} Measured in H$_2$O at 30.0°. ^{c} Approximate value only because of secondary decomposition.

The most significant differences are seen in the infrared absorption spectra. The group VI-B metal complexes each show a single strong absorption band in the C–H stretching region,[7] but the corresponding iron complex shows three strong bands which presumably reflect a lower symmetry of the C$_7$H$_7$ ligand in the iron complex.[8] Furthermore, the group VI-B metal complexes are transparent in the 650–800 cm.$^{-1}$ region while the iron complex shows an intense absorption band at 731 cm.$^{-1}$ suggestive of the presence of a cis double bond.

On the basis of this evidence, we propose that the structure of the tropylium–iron tricarbonyl cation is as shown in IIIa. The iron atom is bonded to five carbons of the ring, leaving one double bond not involved in coordination to the metal. The ligand–metal bonding is then analogous to that found in other pentadienyl–iron tricarbonyl cationic complexes.[9] The pK_{R^+} value of the C$_7$H$_7$–Fe(CO)$_3$ cation is very similar to that of the cycloheptadienyl–iron tricarbonyl cation (see Table I). The salt displays carbonyl absorption typical of dienyl–iron tricarbonyl cations (strong absorption peaks at 2070 and 2120 cm.$^{-1}$).[9]

IIIa   IIIb
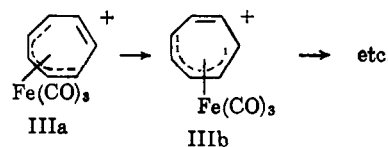
(7) H. P. Fritz, "Advances in Organometallic Chemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1964, p. 240.
(8) ν_{C-H} 3086, 3076, and 3086 cm.$^{-1}$ for the Cr, Mo, and W complexes, respectively, and 3093, 3070, and 3056 cm.$^{-1}$ for the Fe complex measured as hexachlorobutadiene mulls using a Beckman IR-7 spectrometer.
(9) R. Pettit and G. F. Emerson, ref. 7, p. 1.