

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./mole²; *cis*-di-*t*-butylethylene, -36.2 kcal./mole³). 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).

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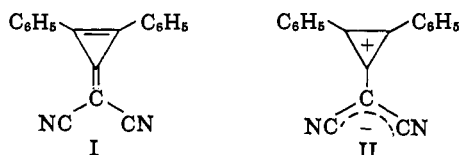
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1-Dicyanomethylene-2,3-diphenylcyclopropene ("1,1-Dicyano-3,4-diphenyltriafulvene")¹

Sir:

Among the nonalternant pseudoaromatic systems that of methylenecyclopropene² ("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 electro-negative substituents as the nitrile group.

Refluxing diphenylcyclopropenone⁷ 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 C₁₈H₁₀N₂: 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 description 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 known⁴⁻⁶ 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 acid¹¹ 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 CDCl₃ (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 m μ (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 m μ (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 H₂SO₄. *Anal.* Calcd. for C₁₈H₁₆N₂O₆S: 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 ± 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 ± 0.02 D. in benzene at 30°), diphenylmethylenemalononitrile (5.85 ± 0.05 D. in benzene at 30°), ω, ω -dicyanodibenzofulvene (5.53 ± 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).

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An Aliphatic Triafulvene¹

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).