

The image of the ir source element (P.E. 137-0032) on the cell, chopped at 5 kHz, is focused by a NaCl lens and spherical front surface mirrors on a Jarrell Ash 0.25-m monochromator containing a 148 g/mm, 5.0 μ blaze grating. The band pass filter output (P.E. 237-1202) is focussed on a Philco-Ford Type GPC201 detector. A tuned preamplifier coupled with a phase-sensitive detector system provides a signal proportional to % T to a storage oscilloscope. Analysis of photographs of oscillographs of % T vs. time was performed with an analog computer as previously described.⁴⁹

Association Measurements. The vapor pressure of ether solu-

tions of cyclopentylmagnesium bromide (base/bromide = 0.8) relative to pure ether at 0° was measured as previously described.⁵¹

Calculations of the fit of various models of the reaction to the experimental data were performed on the PLATO IV computer-based teaching system.⁵² This computer system provides essentially instantaneous interaction with the mathematical model of the system and represents the data with two-dimensional graphics.

(52) D. Alpert and D. L. Bitzer, *Science*, **167**, 1582 (1970).

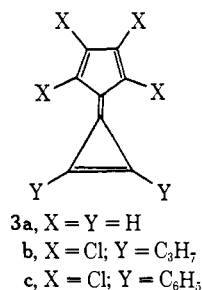
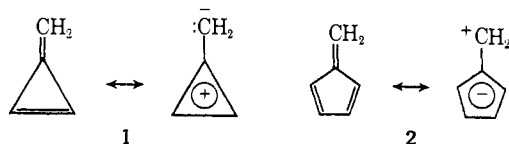
Structures of, and Charge Separation in, 2,3-Diphenyl-4,4-dicyanotriafulvene and 2,3-Diphenylcyclopropenone

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Abstract: The crystal structures of 2,3-diphenyl-4,4-dicyanotriafulvene (CYANOF) and 2,3-diphenylcyclopropenone (PROPEN) have been determined with Mo K X-ray diffraction data. CYANOF crystallizes in the monoclinic space group $A2/a$, with cell parameters of $a = 9.5800$, $b = 10.0791$, $c = 14.2918$ Å, and $\beta = 106.546^\circ$ and $Z = 4$. PROPEN crystallizes as the monohydrate in the orthorhombic space group $Pbca$ with cell parameters of $a = 9.291$, $b = 20.658$, and $c = 25.081$ Å and $Z = 16$. The final R factors were 0.035 for CYANOF and 0.043 for PROPEN after full-matrix least-squares structure refinement. Four least-squares minimization functions were tested with the CYANOF data. CNDO/2 calculations have been carried out to obtain charge density and bond order information. The O charge magnitudes in cyclopropenones are 0.12–0.14 e larger than the corresponding charges in saturated ketones. There is a larger negative charge on O in PROPEN (-0.387) than on the $C(CN)_2$ group in CYANOF (-0.366), but the positive charge distributions in the remainder of the molecules place more of the charge on the CYANOF phenyl than on the PROPEN phenyl. This result is in accord with the relative ¹⁹F nmr chemical shifts of 2,3-di(*p*-fluorophenyl)-4,4-dicyanotriafulvene and 2,3-di(*p*-fluorophenyl)cyclopropenone.

The fulvenes are nonalternant hydrocarbons which can formally reach Hückel aromatic status by the shift of a π -electron pair either toward, or away from, an unsaturated ring. Mesomeric structures such as the two π -electron cyclopropenium form of triafulvene (1)¹ and the six π -electron cyclopentadienide form of

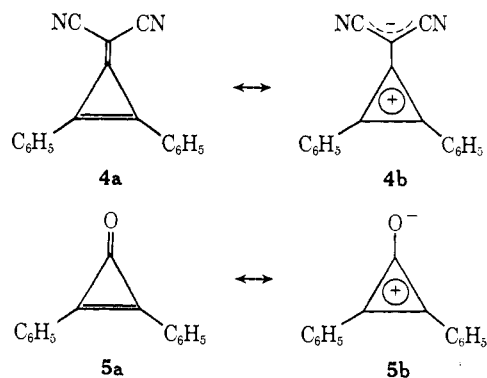


pentafulvene (2)¹ have intrigued chemists for years with the promise of pseudoaromatic character. The three-ring donor and five-ring acceptor can be joined

(1) The "Chemical Abstracts" names of these compounds are cyclopropenyliidenemethane for 1 and cyclopentadienyliidenemethane for 2.

to form a fulvalene, an example of which is pentatriafulvene (3a, calicene).

Many attempts have been made to increase the ground state dipolarities of these compounds by the substitution of electron withdrawing groups for H (a) on the rings of acceptor fulvenes and (b) on the methylene carbons exocyclic to the rings of donor fulvenes. As part of a program to identify the structural consequences of charge separation, the structure of a compound of type b, viz., 2,3-diphenyl-4,4-dicyanotriafulvene (4) (CYANOF; 2,3-diphenyl-2-cyclopropene- $\Delta^{1,\alpha}$ -malononitrile), and the structure of the corresponding ketone (5) (PROPEN, 2,3-diphenylcyclopropenone) have been investigated. The pair of struc-



tures was determined to permit an evaluation of the relative electron withdrawing ability of oxygen *vs.* dicyanomethylene. In this paper, we report the X-ray crystal structures of CYANOF and PROPEN, the results of CNDO/2 calculations on the compounds, and what these data indicate about dipolar character.

Experimental Section

2,3-Diphenyl-4,4-dicyanotriafulvene (4) was prepared from the β -aminoalanine catalyzed condensation of 2,3-diphenylcyclopropenone and malononitrile in acetic anhydride,² and crystals were grown by the slow evaporation of an acetonitrile solution (mp 287–289° (lit. 288–290°)). The compound readily formed large blocks several millimeters in maximum dimension which were orange-tan in color. Smaller crystals appeared light yellow.

2,3-Diphenylcyclopropenone (5) was synthesized using the method of Breslow and Posner.³ Recrystallization of the crude reaction product from cyclohexane, without drying *in vacuo* or in air for an extended period of time, gave large, colorless crystals of the monohydrate. The melting point of the hydrate was 87–90° (lit.⁴ 87.5°) while that of the dried material was 118–120° (lit.³ 119–120°). Suitable X-ray diffraction specimens of the latter material could not be obtained and, therefore, the hydrate was used in these investigations. The hydrate diffraction samples were enclosed in glass capillaries to prevent loss of water. **Caution.** Two undergraduates who worked with diphenylcyclopropenone in my laboratory experienced severe allergic reactions³ to the compound. They both received a rash of large water-filled blisters on the hands and arms resembling a bad case of poison ivy.

General X-ray Diffraction Experimental. A preliminary photographic survey of each material was made to establish the Laue symmetry, identify the systematic absences for space group determination, and provide rough values of the lattice constants. Final cell parameter and intensity measurements were made using a Picker FACS-I diffractometer equipped with a Mo K α , λ 0.71069 Å; monochromator $2\theta = 12.16^\circ$, scintillation detector, pulse height analyzer, disk for program storage, and magnetic tape for data output. Cell constants were obtained by the method of least squares using 2θ values determined from manual measurements of $+2\theta$ and -2θ for each reflection. The intensity data were collected using the $\theta-2\theta$ scan method with background measurements made at the beginning and end of each scan; the 2θ scan range was calculated from $A + 0.692 \tan \theta$, where A describes the basic reflection width. Three standard reflection intensities, monitored at 50–100 reflection intervals, were used to correct for intensity fluctuations and to determine a value for the "instability factor."⁵ Foil attenuators were automatically inserted during the intensity measurements to keep the maximum count rate below ca. 15,000 counts sec⁻¹. The reflection intensities (I) and standard deviations ($\sigma(I)$) were calculated using the following equations

$$I = SA(I_s - K(I_{B1} + I_{B2}))$$

and

$$\sigma(I) = (S^2 A^2 (I_s + K^2 (I_{B1} + I_{B2})) + DC^2)^{1/2}$$

where I_s is the scan intensity, I_{B1} and I_{B2} are the two background values, K is the ratio (scan time)/(total background time), A is the attenuator factor, $C = I_s + I_{B1} + I_{B2}$, D is the instability factor, and S is the reflection scale factor determined from the standard intensity data. The crystal densities were measured by the neutral buoyancy (flotation) method in aqueous KI.

The crystal data and the diffraction intensity information are summarized in Tables I and II.

Intensity corrections were made for intensity fluctuations and crystal decomposition and for Lp . Absorption corrections were not made.

Structure determination was by direct methods. For PROPEN, an E map computed with 470 reflections (239+, 231-) revealed the 34 C and O atoms. For CYANOF, an E map computed with 137 reflections (71+, 66-) revealed the 11 C and N atoms. All H atoms were located from difference maps.

Refinement was by full-matrix least squares using anisotropic

(2) S. Andreades, *J. Amer. Chem. Soc.*, **87**, 3941 (1965).

(3) R. Breslow and J. Posner, *Org. Syn.*, **47**, 62 (1967).

(4) F. Toda and A. Katsuhiko, *Tetrahedron Lett.*, 3735 (1968).

(5) G. H. Stout and L. H. Jensen, "X-ray Structure Determination. A Practical Guide," Macmillan, New York, N. Y., 1968, p 456.

Table I. Crystal Data

	2,3-Diphenylcyclopropenone	2,3-Diphenyl-4,4-dicyanotriafulvene
Molecular formula	C ₁₇ H ₁₀ O · H ₂ O	C ₁₅ H ₁₀ N ₂
Space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>A2/a</i>
Unit cell parameters (esd's in parentheses)	$a = 9.291(1)$, $b = 20.658(3)$, $c = 25.081(5)$ Å	$a = 9.5800(6)$, $b = 10.0791(6)$, $c = 14.2918(9)$ Å; $\beta = 106.546(7)^\circ$
Av of $ 2\theta_o - 2\theta_e $	0.003°	0.002°
Z	16 (2 molecules per asymmetric unit)	4 (on crystallographic C ₂ axis)
V	4814 Å ³	1323 Å ³
ρ_{measured}	1.202 g cm ⁻³	1.276 g cm ⁻³
$\rho_{\text{X-ray}}$	1.237 g cm ⁻³	1.277 g cm ⁻³

Table II. Intensity Information

	2,3-Diphenylcyclopropenone	2,3-Diphenyl-4,4-dicyanotriafulvene
Crystal dimensions	0.5 × 0.5 × 0.5 mm	0.12 × 0.12 × 0.25 mm
Reciprocal lattice vector parallel to diffractometer ϕ axis	[4,0,0]	[2,0,6]
2θ scan rate	2° min ⁻¹	0.5° min ⁻¹
Reflection width, Å	1.5°	1.6°
Time for each background	10 sec	40 sec
Maximum 2θ (sin θ/λ) for intensity measurement	50.0° (0.5947)	50.1° (0.5958)
Instability factor, D	0.000088	0.00011
Total data measured including standards and duplicate reflections	5095	1374
Total unique data (observed data)	4241 (2130)	1162 (710)

temperature factors for C, N, and O and isotropic terms for H. The form of the anisotropic terms given in Tables III and V is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$. The F_o 's were corrected for isotropic secondary extinction (r^*) using eq 22 given by Larson.⁶ The "unobserved" data were included in the calculations only in those cases in which I_o was greater than $3\sigma(I_o)$.

PROPEN. The function minimized in the structure refinement was $\sum w(F_o - F_c)^2$ where $w = [1/\sigma(F)]^2$. Because program limitations did not permit the simultaneous refinement of all of the 402 C, O, and H positional and thermal parameters, a "full" refinement cycle consisted of refining 23 of the C and O atoms (the maximum number) for one cycle, followed by a second cycle in which the remaining 11 C and O atoms plus 12 of the original 23 atoms selected at random were refined. The initial set of 23 atoms from one "full" cycle to another was always different. The H atoms were refined separately for two cycles following every two "full" cycles of C and O refinement. The final agreement factor ($R = \sum |F_o - F_c|/\sum F_o$) was 0.043 and the weighted factor (wtd $R = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$) was 0.023. The atomic parameters and structure factors are given in Tables III and IV.⁷

CYANOF. The structure was refined using four least-squares minimization functions, the results of which are outlined in the Discussion. The atomic parameters and structure factors from the $\sum [1/\sigma(F)]^2 [F_o - F_c]^2$ refinement are listed in Tables V and VI.⁷ The R and wtd R factors are 0.035 and 0.026.

f Curves. C, N, and O are from Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Venedaal⁸ and H from Stewart, Davidson, and Simpson.⁹

(6) A. C. Larson, "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, Denmark, 1970, p 291.

(7) See paragraph at end of paper regarding supplementary material.

(8) J. Berghuis, I. J. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Venedaal, *Acta Crystallogr.*, **8**, 478 (1955).

(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table III. Atomic Fractional Coordinates, Temperature (\AA^2), and Extinction Factors for 2,3-Diphenylcyclopropenone^a

Atom	X	Y	Z	U or U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O	0.1381 (2)	0.08196 (9)	-0.03681 (7)	0.038 (1)	0.062 (1)	0.083 (1)	-0.003 (1)	-0.007 (1)	-0.011 (1)
C(1)	0.2639 (3)	0.0955 (1)	-0.0263 (1)	0.058 (2)	0.046 (2)	0.050 (2)	0.004 (2)	0.003 (2)	0.002 (1)
C(2)	0.3672 (3)	0.1336 (1)	-0.0001 (1)	0.046 (2)	0.046 (2)	0.046 (2)	0.001 (2)	0.001 (2)	0.001 (1)
C(3)	0.4136 (3)	0.0855 (1)	-0.0323 (1)	0.043 (2)	0.050 (2)	0.047 (2)	0.000 (2)	0.000 (2)	0.001 (1)
C(1a)	0.3980 (3)	0.1884 (1)	0.03439 (9)	0.049 (2)	0.050 (2)	0.042 (1)	0.001 (1)	0.001 (1)	0.001 (1)
C(2a)	0.2838 (3)	0.2195 (1)	0.0596 (1)	0.047 (2)	0.068 (2)	0.062 (2)	0.000 (2)	-0.004 (2)	-0.008 (2)
C(3a)	0.3072 (3)	0.2739 (1)	0.0906 (1)	0.060 (2)	0.075 (2)	0.067 (2)	0.007 (2)	0.002 (2)	-0.017 (2)
C(4a)	0.4454 (4)	0.2975 (1)	0.0969 (1)	0.074 (2)	0.058 (2)	0.053 (2)	-0.004 (2)	-0.005 (2)	-0.009 (2)
C(5a)	0.5596 (3)	0.2665 (1)	0.0729 (1)	0.057 (2)	0.059 (2)	0.063 (2)	-0.009 (2)	-0.009 (2)	-0.003 (2)
C(6a)	0.5377 (3)	0.2117 (1)	0.0421 (1)	0.051 (2)	0.055 (2)	0.058 (2)	-0.001 (2)	0.003 (2)	0.000 (2)
C(1b)	0.5338 (3)	0.0504 (1)	-0.0557 (1)	0.041 (2)	0.047 (2)	0.046 (2)	-0.002 (1)	0.002 (1)	0.002 (1)
C(2b)	0.5096 (3)	-0.0001 (1)	-0.0914 (1)	0.043 (2)	0.060 (2)	0.052 (2)	-0.006 (1)	-0.002 (1)	-0.005 (1)
C(3b)	0.6239 (3)	-0.0341 (1)	-0.1124 (1)	0.057 (2)	0.063 (2)	0.059 (2)	0.001 (2)	0.003 (2)	-0.014 (2)
C(4b)	0.7633 (3)	-0.0183 (1)	-0.0980 (1)	0.055 (2)	0.071 (2)	0.062 (2)	0.008 (2)	0.007 (2)	-0.011 (2)
C(5b)	0.7896 (3)	0.0316 (1)	-0.0627 (1)	0.042 (2)	0.071 (2)	0.080 (2)	0.001 (2)	-0.001 (2)	-0.012 (2)
C(6b)	0.6751 (3)	0.0661 (1)	-0.0411 (1)	0.053 (2)	0.054 (2)	0.065 (2)	0.002 (2)	0.000 (2)	-0.012 (2)
O'	0.0746 (2)	-0.2609 (1)	-0.09345 (7)	0.086 (2)	0.091 (2)	0.046 (1)	0.017 (1)	0.004 (1)	-0.007 (1)
C(1')	0.0823 (3)	-0.2634 (1)	-0.1420 (1)	0.054 (2)	0.066 (2)	0.057 (2)	-0.002 (2)	0.001 (2)	-0.002 (2)
C(2')	0.1327 (3)	-0.2931 (1)	-0.1891 (1)	0.055 (2)	0.055 (2)	0.053 (2)	-0.005 (2)	-0.001 (2)	-0.004 (2)
C(3')	0.0485 (3)	-0.2397 (1)	-0.1932 (1)	0.056 (2)	0.055 (2)	0.055 (2)	-0.001 (2)	0.001 (2)	-0.002 (2)
C(1a')	0.2193 (3)	-0.3429 (1)	-0.2145 (1)	0.053 (2)	0.051 (2)	0.053 (2)	-0.004 (2)	-0.002 (2)	-0.003 (2)
C(2a')	0.2858 (3)	-0.3897 (1)	-0.1835 (1)	0.074 (2)	0.065 (2)	0.051 (2)	-0.004 (2)	0.003 (2)	0.001 (2)
C(3a')	0.3713 (3)	-0.4373 (1)	-0.2066 (1)	0.080 (2)	0.059 (2)	0.069 (2)	0.008 (2)	-0.006 (2)	0.001 (2)
C(4a')	0.3894 (3)	-0.4372 (1)	-0.2615 (1)	0.075 (2)	0.054 (2)	0.077 (2)	0.004 (2)	0.008 (2)	-0.010 (2)
C(5a')	0.3228 (4)	-0.3913 (1)	-0.2927 (1)	0.093 (3)	0.068 (2)	0.055 (2)	0.010 (2)	0.009 (2)	-0.004 (2)
C(6a')	0.2384 (3)	-0.3440 (1)	-0.2697 (1)	0.074 (2)	0.060 (2)	0.054 (2)	0.011 (2)	0.000 (2)	0.000 (2)
C(1b')	-0.0248 (3)	-0.1926 (1)	-0.2263 (1)	0.057 (2)	0.052 (2)	0.058 (2)	0.001 (2)	0.003 (2)	-0.001 (1)
C(2b')	-0.0846 (4)	-0.1386 (1)	-0.2030 (1)	0.112 (3)	0.082 (2)	0.054 (2)	0.033 (2)	0.006 (2)	-0.004 (2)
C(3b')	-0.1549 (4)	-0.0924 (2)	-0.2333 (1)	0.116 (3)	0.090 (3)	0.071 (2)	0.042 (2)	0.014 (2)	0.006 (2)
C(4b')	-0.1688 (3)	-0.1014 (1)	-0.2877 (1)	0.076 (2)	0.076 (2)	0.070 (2)	0.009 (2)	0.000 (2)	0.014 (2)
C(5b')	-0.1094 (3)	-0.1550 (1)	-0.3113 (1)	0.090 (3)	0.071 (2)	0.057 (2)	-0.002 (2)	-0.004 (2)	0.000 (2)
C(6b')	-0.0367 (3)	-0.2003 (1)	-0.2810 (1)	0.084 (2)	0.062 (2)	0.056 (2)	0.007 (2)	0.001 (2)	-0.006 (2)
O(w1)	0.1434 (2)	-0.03342 (9)	-0.10227 (7)	0.081 (2)	0.075 (1)	0.071 (1)	-0.007 (1)	0.009 (1)	-0.005 (1)
O(w2)	0.0772 (2)	-0.14069 (9)	-0.03810 (8)	0.094 (2)	0.082 (1)	0.101 (2)	-0.021 (1)	0.024 (1)	-0.007 (1)
H(2a)	0.188 (2)	0.2029 (8)	0.0549 (7)	0.054 (6)					
H(3a)	0.219 (2)	0.293 (1)	0.1084 (8)	0.098 (8)					
H(4a)	0.459 (2)	0.3402 (9)	0.1195 (8)	0.069 (7)					
H(5a)	0.663 (2)	0.2811 (9)	0.0796 (7)	0.068 (7)					
H(6a)	0.621 (2)	0.1889 (9)	0.0228 (8)	0.079 (8)					
H(2b)	0.411 (2)	-0.0120 (8)	-0.1009 (7)	0.046 (6)					
H(3b)	0.605 (2)	-0.0719 (9)	-0.1376 (7)	0.060 (6)					
H(4b)	0.847 (2)	-0.0421 (9)	-0.1152 (8)	0.079 (7)					
H(5b)	0.890 (2)	0.0434 (9)	-0.0514 (8)	0.080 (8)					
H(6b)	0.689 (2)	0.1038 (9)	-0.0131 (7)	0.067 (7)					
H(2a')	0.268 (2)	-0.3912 (8)	-0.1457 (7)	0.049 (6)					
H(3a')	0.420 (3)	-0.472 (1)	-0.1791 (9)	0.12 (1)					
H(4a')	0.447 (2)	-0.471 (1)	-0.2784 (8)	0.085 (8)					
H(5a')	0.343 (2)	-0.3956 (9)	-0.3305 (8)	0.088 (8)					
H(6a')	0.193 (2)	-0.308 (1)	-0.2918 (8)	0.089 (8)					
H(2b')	-0.075 (2)	-0.134 (1)	-0.1655 (8)	0.083 (8)					
H(3b')	-0.198 (3)	-0.054 (1)	-0.216 (1)	0.14 (1)					
H(4b')	-0.221 (2)	-0.0680 (9)	-0.3098 (8)	0.081 (8)					
H(5b')	-0.123 (2)	-0.165 (1)	-0.3508 (9)	0.109 (9)					
H(6b')	0.003 (2)	-0.241 (1)	-0.2987 (8)	0.087 (8)					
H(wa)	0.130 (3)	-0.067 (1)	-0.084 (1)	0.12 (1)					
H(wb)	0.142 (3)	-0.001 (1)	-0.083 (1)	0.13 (1)					
H(wc)	0.011 (4)	-0.126 (2)	-0.028 (1)	0.19 (1)					
H(wd)	0.073 (3)	-0.174 (1)	-0.051 (1)	0.15 (1)					

^a Estimated standard deviations are given in parentheses. $r^* = 0.0229 (3)$.

Computer Programs. PDP-8i: P. G. Lenhert's disk control system for the Picker FACS-I diffractometer.¹⁰ UNIVAC 1108: J. M. Stewart's *X-ray system*;¹¹ CNINDO (QCPE No. 141) for the CNDO/2 calculations.¹²

Discussion

Structure Refinement of CYANOF. The relatively small number of atomic parameters (111) and reflections

(10) P. G. Lenhert and D. Henry, Abstracts, ACA Meeting, New Orleans, La., Spring 1970, p 71.

(11) "The X-ray System-Version of June 1972," Technical Report 192, Computer Science Center, University of Maryland, 1972.

(12) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(1162) for this structure made it economically possible to experiment with four minimization functions for least-squares structure refinement. These functions were: (1) $\Sigma[F_o - F_c]^2$; (2) $\Sigma[1/\sigma(F)]^2[F_o - F_c]^2$; (3) $\Sigma[F_o^2 - F_c^2]^2$; (4) $\Sigma[1/\sigma(F^2)]^2[F_o^2 - F_c^2]^2$. Function 4 is equivalent to the weighed intensity function, $\Sigma[1/\sigma(I)]^2[I_o - I_c]^2$, because of cancellation of the Lp terms in $\sigma(I)$ and I .¹³ Most of the differences in the atomic

(13) The $\Sigma(I_o - I_c)^2$ function was also tested, but with disastrous results; for example, very large H temperature factors, nonpositive definite temperature factors for two C's, positional σ 's approximately ten times larger than those obtained with the other functions, atomic positions which gave completely erroneous bond lengths and angles.

Table V. Atomic Fractional Coordinates, Temperature (\AA^2), and Extinction Factors for 2,3-Diphenyl-4,5-dicyanotriafulvene^a

	X	Y	Z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.2500	0.8756 (3)	0.5000	0.041 (1)	0.051 (2)	0.048 (2)	0.000	0.007 (1)	0.000
C(2)	0.1830 (2)	0.7540 (2)	0.4683 (1)	0.042 (1)	0.055 (1)	0.051 (1)	0.000 (1)	0.006 (1)	0.000 (1)
C(4)	0.2500	1.0112 (2)	0.5000	0.042 (1)	0.043 (1)	0.055 (2)	0.000	0.003 (1)	0.000
C(5)	0.1275 (2)	1.0828 (2)	0.4422 (1)	0.053 (1)	0.046 (1)	0.060 (1)	-0.001 (1)	0.011 (1)	-0.004 (1)
C(6)	0.0578 (2)	0.6852 (2)	0.4072 (1)	0.041 (1)	0.046 (1)	0.047 (1)	0.000 (1)	0.005 (1)	-0.002 (1)
C(7)	0.0596 (2)	0.5482 (2)	0.3980 (1)	0.050 (1)	0.051 (1)	0.065 (1)	0.003 (1)	-0.001 (1)	-0.003 (1)
C(8)	-0.0580 (2)	0.4830 (2)	0.3368 (2)	0.064 (1)	0.050 (1)	0.077 (2)	-0.004 (1)	-0.005 (1)	-0.009 (1)
C(9)	-0.1778 (2)	0.5539 (2)	0.2861 (1)	0.052 (1)	0.067 (1)	0.068 (1)	-0.013 (1)	-0.003 (1)	-0.014 (1)
C(10)	-0.1825 (2)	0.6890 (2)	0.2954 (1)	0.045 (1)	0.066 (1)	0.072 (1)	0.004 (1)	-0.009 (1)	-0.003 (1)
C(11)	0.0643 (2)	0.7550 (2)	0.3553 (1)	0.051 (1)	0.047 (1)	0.070 (1)	0.004 (1)	-0.001 (1)	-0.004 (1)
N	0.0277 (2)	1.1389 (2)	0.3954 (1)	0.066 (1)	0.066 (1)	0.080 (1)	0.013 (1)	0.003 (1)	0.005 (1)
H(7)	0.145 (2)	0.499 (1)	0.437 (1)	0.057 (5)					
H(8)	-0.053 (2)	0.383 (2)	0.333 (1)	0.084 (6)					
H(9)	-0.261 (2)	0.507 (1)	0.241 (1)	0.064 (5)					
H(10)	-0.268 (2)	0.739 (1)	0.261 (1)	0.072 (6)					
H(11)	-0.065 (2)	0.850 (1)	0.364 (1)	0.054 (5)					

^a Estimated standard deviations are given in parentheses. $r = 0.0049 (1)$.

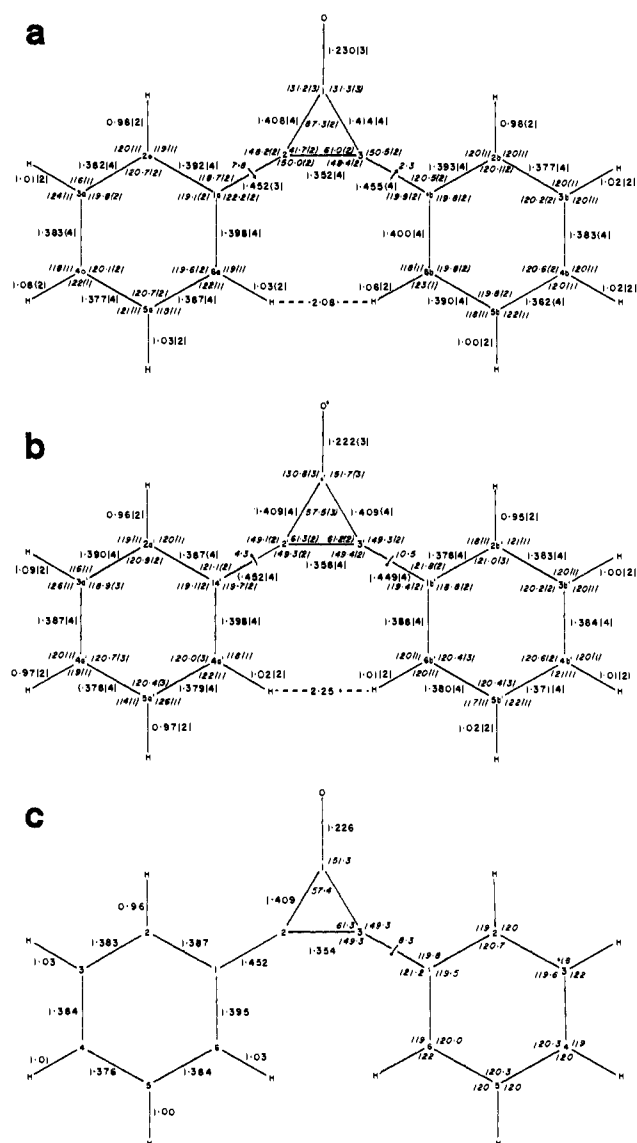


Figure 1. Bond lengths (\AA) and angles (deg) for 2,3-diphenylcyclopropenone. Estimated standard deviations are given in parentheses: (a) unprimed molecule; (b) primed molecule; (c) average.

parameters were 1σ or less. There were five 2σ , one 3σ , and one 4σ differences. The four functions gave

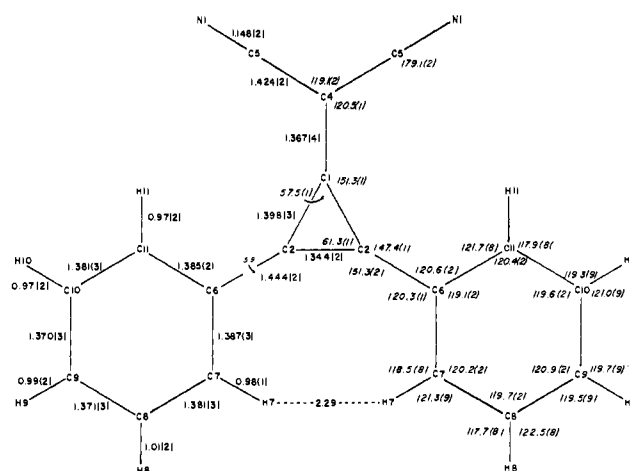


Figure 2. Bond lengths (\AA) and angles (deg) for 2,3-diphenyl-4,4-dicyanotriafulvene. Estimated standard deviations are given in parentheses.

two distinct sets of atomic, scale, and extinction parameters. The parameters from the unit weighted functions, 1 and 3, were virtually identical and formed one set, while the σ weighted functions, 2 and 4, formed the second set. The extinction factors from the unit and σ weighted refinements showed the largest differences, $7\text{--}20\sigma$. The factors were largest in the σ weighted calculations since extinction effects are most important for the large, low order reflections, and it is just these data whose relative weights are increased by a σ weighted function. The C and N temperature factors from the unit weighted refinements were smaller than the corresponding σ weighted parameters; the opposite effect was observed for the H temperature factors. The σ weights, in general, gave slightly smaller parameter standard deviations. The agreement factors (R) are given in Table VII.

The Structures of CYANOF and PROPEN. Bond lengths and angles for these compounds are given in Figures 1 and 2. The unique structural unit in CYANOF consists of only one-half of the molecule depicted in Figure 2 because of the coincidence of the molecular C_2 axis with a crystallographic C_2 axis. The molecular packing in CYANOF is straightforward, with no intermolecular distances less than van der Waals distances.

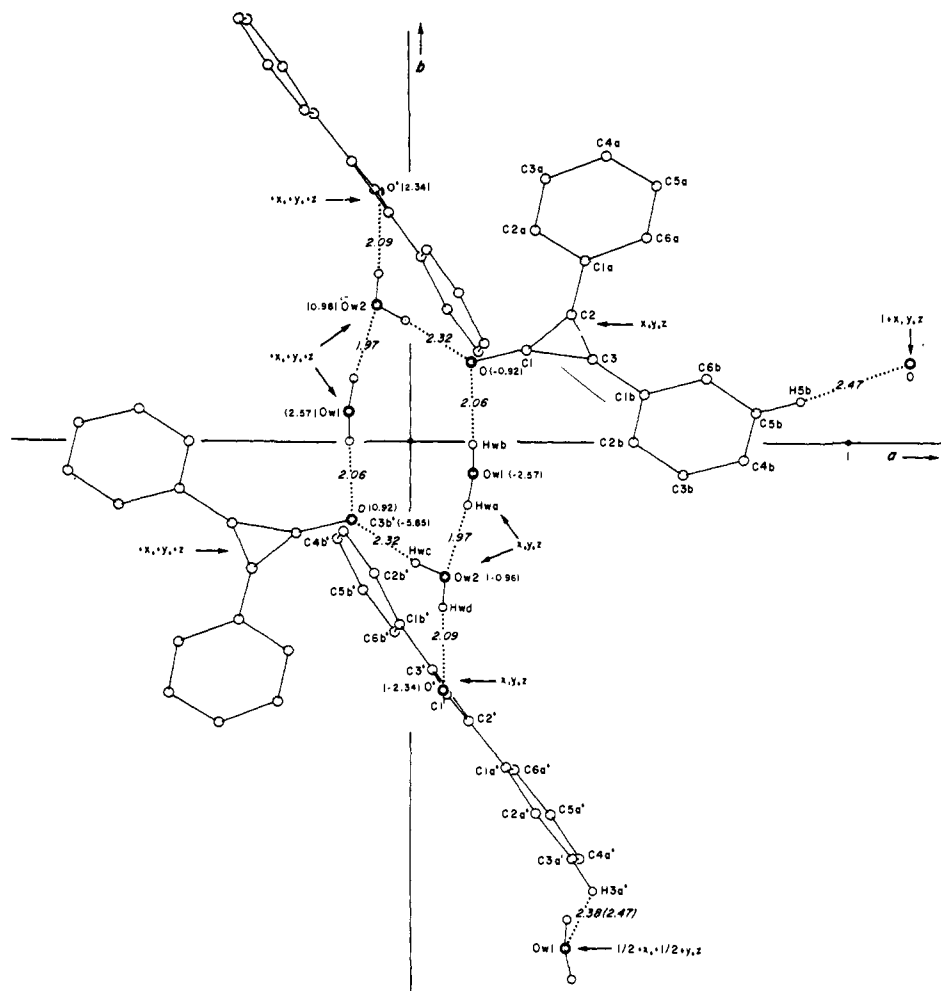


Figure 3. Intermolecular packing diagram for 2,3-diphenylcyclopropenone illustrating the water-PROPEN hydrogen-bonded structure. Distances and several atomic heights (in parentheses) above the ab plane are given in Å. The view is down c .

Table VII. R Factors for the Four Refinement Functions Used with CYANOF

	Function			
	1	2	3	4
R (on F)	0.034 ^a	0.035	0.035	0.035
wtd R (on F)	0.031 ^b	0.026 ^a	0.031 ^b	0.075
R (on F^2)	0.038	0.048	0.037 ^a	0.048
wtd R (on F^2)				0.050 ^a

^a R factors most appropriate to the functions. ^b Weights = 1.

There are two crystallographically unique molecules of diphenylcyclopropenone. The packing for PROPEN is dominated by a hydrogen-bonded structure, consisting of four water molecules and two diphenylcyclopropenones, arranged about a center of symmetry (Figure 3). The center relates the two cyclopropenones and the two crystallographically unique pairs of water molecules. Both H atoms, Hwa and Hwb, of water number 1, but only Hwc of water number 2, are used within the water-cyclopropenone structure. The fourth water H atom, Hwd, is linked to the second crystallographically unique cyclopropenone.

The cyclopropenone moiety and the two phenyl C's attached to the three-ring are coplanar (Table VIII) in each of the PROPEN molecules; the dicyanotriafulvene portion plus the two three-ring C substituents are coplanar (Table IX) in CYANOF; the four PROPEN

and one CYANOF benzene rings are individually planar. The twist angles between the benzene and three-ring planes average 6.2° in PROPEN and 5.9° in CYANOF. The $H \cdots H$ contacts illustrated in Figures 1 and 2 are probably responsible for the directions of phenyl twist, which locate the H atoms on opposite sides of the three-rings.

The analysis of the structural features of three-ring compounds is limited by the relatively small amount of available structural data (bond lengths, angles) and because bond lengths from other cyclic and acyclic molecules are inappropriate standards for cyclopropanes and cyclopropenes. In general, single and double bonds in three-rings, and single bonds linked to three-rings, can be as much as 0.03–0.05 Å shorter than normal values for these kinds of connections.¹⁴ This same type of shortening probably also applies to double bonds exocyclic to the three-rings.^{16,17}

(14) Unusually long C–C distances have been reported for several saturated three-ring compounds: for example, 1.575 Å in cyclopropanone (ref 15); 1.60 Å in *cis*-2,3-dimethylthiirane 1,1-dioxide (R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967)); 1.590 Å in thirane 1,1-dioxide (Y. Nakano, S. Saito, and Y. Morino, *Bull. Chem. Soc. Jap.*, **43**, 368 (1970)).

(15) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **91**, 1896 (1969).

(16) W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).

(17) The C=C distances in methylenecyclopropane (1.332 Å; V. W. Laurie and W. M. Stigliani, *J. Amer. Chem. Soc.*, **92**, 1485 (1970)) and triisopropylidenecyclopropane (1.36 Å, ref 18) are respectively the

Table VIII. Least-Squares Planes and Deviations (Å) for 2,3-Diphenylcyclopropenone

	Plane		
	1	2	3
C(1)	0.0 ^a	-0.265	0.086
C(2)	0.0 ^a	-0.085	0.030
C(3)	0.0 ^a	-0.110	0.035
O	-0.017	-0.448	0.123
C(1a)	-0.049	-0.012 ^a	-0.439
C(2a)	0.044	0.006 ^a	0.065
C(3a)	-0.068	0.004 ^a	-0.079
C(4a)	-0.265	-0.006 ^a	-0.336
C(5a)	-0.337	-0.001 ^a	-0.056
C(6a)	-0.217	0.010 ^a	-0.283
C(1b)	-0.008	-0.038	-0.002 ^a
C(2b)	-0.039	-0.180	0.000 ^a
C(3b)	-0.012	-0.077	0.000 ^a
C(4b)	0.049	0.171	0.000 ^a
C(5b)	0.080	0.314	-0.002 ^a
C(6b)	0.057	0.216	0.002 ^a

Plane 1: $-0.0920x - 13.0740y + 19.4177z = -1.7824$

Plane 2: $1.0451x - 11.9938y + 20.2253z = -1.1356$

Plane 3: $-0.4630x - 13.3337y + 19.1164z = -1.9831$

C(1')	0.0 ^a	0.125	-0.165
C(2')	0.0 ^a	0.026	0.092
C(3')	0.0 ^a	0.043	-0.169
O'	-0.002	0.213	-0.366
C(1a')	0.045	0.003 ^a	0.357
C(2a')	0.005	-0.002 ^a	0.301
C(3a')	0.069	-0.002 ^a	0.573
C(4a')	0.177	0.005 ^a	0.905
C(5a')	0.205	-0.004 ^a	0.951
C(6a')	0.145	0.000 ^a	0.686
C(1b')	-0.008	-0.004	-0.004 ^a
C(2b')	0.199	0.266	-0.006 ^a
C(3b')	0.203	0.235	0.011 ^a
C(4b')	-0.040	-0.106	-0.006 ^a
C(5b')	-0.245	-0.375	-0.003 ^a
C(6b')	-0.221	-0.316	0.008 ^a

Plane 1: $7.5674x + 11.9771y + 0.5501z = -2.6105$

Plane 2: $7.4397x + 12.2213y + 2.3573z = -3.0672$

Plane 3: $7.9646x + 10.2613y - 3.4055z = -1.3988$

^a Atom used for definition of the plane.

The standard lengths of the C=C and =C-C= linkages in the three-membered rings are probably close to the 1.30 Å in cyclopropene²⁰ and the 1.44 Å in triisopropylidenecyclopropane.¹⁸ The mean of these distances, 1.37 Å, is near the 1.373-Å three-ring length in trisphenylcyclopropenium perchlorate²¹ and the 1.363-Å distance in tris(dimethylamino)cyclopropenium perchlorate.²² The 1.373-Å value, which has been cited frequently as the standard length for the completely delocalized cyclopropenium connection, is 0.02–0.03 Å less than the benzene C-C distance. The single and double bond averages in CYANOF and PROPEN, respectively, 1.371 and 1.382 Å, are close to the cyclopropenium value, and the small differences between the C-C and C=C lengths and their respective means, 0.027 Å for CYANOF and 0.028 Å in PROPEN, sug-

same as and larger than the usual ethylenic distance, whereas the 1.191 Å C=O distance in cyclopropanone (ref 15) is about 0.02 Å shorter than the 1.212 Å distance in acetone (ref 19).

(18) H. Dietrich and H. Dierks, *Angew. Chem., Int. Ed. Engl.*, **7**, 465 (1968).

(19) T. Iijima, *Bull. Chem. Soc. Jap.*, **43**, 1049 (1970).

(20) (a) P. H. Kasai, R. J. Myers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959); (b) J. F. Chiang, *J. Chin. Chem. Soc.*, **17**, 65 (1970).

(21) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).

(22) A. N. Ku and M. Sundaralingam, *ibid.*, **94**, 1688 (1972).

Table IX. Least-Squares Planes and Deviations (Å) for 2,3-Diphenyl-4,4-dicyanotriafulvene

	Plane	
	1	2
C(1)	0.0 ^a	-0.167
C(2)	0.0 ^a	-0.042
C(3) ^b	0.0 ^a	-0.042
C(4)	0.000	-0.307
C(5)	-0.001	-0.385
N	0.004	-0.440
C(6)	-0.030	-0.003 ^a
C(7)	-0.165	0.005 ^a
C(8)	-0.236	0.000 ^a
C(9)	-0.164	-0.006 ^a
C(10)	-0.011	0.007 ^a
C(11)	0.046	-0.003 ^a

Plane 1: $-6.1739x + 0.0021y + 13.0986z = 5.0077$

Plane 2: $-6.1266x - 1.0352y + 13.0407z = 4.2489$

^a Atom used for definition of the plane. ^b Related to C(2) by the crystallographic twofold axis.

gest that the three-rings have some cyclopropenium character.

A recent microwave study of cyclopropenone²³ reported C=O and C-C distances of 1.212 and 1.412 Å, which are in good agreement with the 1.226- and 1.409-Å PROPEN values. These carbonyl distances are 0.02–0.03 Å longer than the 1.191-Å length in cyclopropanone¹⁵ and indicate enhanced carbon-oxygen single bond character in the unsaturated compounds. The ca. 0.05-Å difference between the C=C distances in cyclopropenone and PROPEN, 1.302²³ and 1.354 Å, may be associated with an effect of the three-ring phenyl substituents in PROPEN.

The three-ring bond lengths in CYANOF and PROPEN are close to those found in 2,3-diphenylcyclopropenethione²⁴ and 8-cyano-8-(2,3-diphenylcyclopropenyl)heptafulvenylium fluoroborate.²⁵ Contrary to the conclusions of the cyclopropenethione investigators, we believe the three-ring distances support a significant contribution of a cyclopropenium thioxide form to the ground state resonance hybrid. Bond distances reported for 2,3-di(*p*-chlorophenyl)cyclopropenone,²⁶ e.g., C=C = 1.48 and C=O = 1.30 Å, must be regarded as erroneous.

Charge Separation. Tobey²⁷ has argued that a dipole moment of 2.8 ± 0.2 D is a property of the carbonyl group itself and that the enhanced moments observed in cyclopropenones (4.7 – 5.1 D) merely reflect the increased distance between the centers of negative (oxygen atom) and positive (middle of three ring)

(23) R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *ibid.*, **95**, 2772 (1973).

(24) L. L. Reed and J. P. Schaefer, *Chem. Commun.*, 528 (1972): the three-ring C-C and C=C bond lengths are 1.403 and 1.338 Å, respectively. The average of these distances is 1.370 Å. The C=S distance of 1.630 Å is substantially longer than the pure carbon-sulfur double bond length, 1.56 Å (N. Trinajstić, *Tetrahedron Lett.*, 1529 (1968)). The C-S π -bond order is 0.73 from Trinajstić's bond order-bond length curve. The CNDO/2 π -bond order for diphenylcyclopropenone (entry E, Table X) is 0.78.

(25) C. Kabuto, M. Oda, and Y. Kitahara, *Tetrahedron Lett.*, 4851 (1972): the three-ring C-C and C=C lengths are 1.398, 1.403 and 1.353 Å, respectively. The average of the single and double lengths is 1.375 Å.

(26) K. Peters and H. G. von Schnering, *Chem. Ber.*, **106**, 935 (1973): C=C = 1.48, C-C = 1.42, C=O = 1.30 Å.

(27) S. W. Tobey, "The Jerusalem Symposia on Quantum Chemistry and Biochemistry III. Aromaticity, Pseudo-Aromaticity and Anti-Aromaticity," E. D. Bergmann and B. Pullman, Ed., Academic Press, New York, N. Y., 1971, p 351.

Table X. CNDO Summary

Compound	Structural parameters	μ_{calcd} (D)	μ_{exptl} (D)	q_{O}	q_{C}	C=O ^c bond order	C=C ^c bond order
A. Acetone	Ref 19, C=O = 1.2122 Å, methyls and C=O eclipsed	3.03	2.85 ²⁸	-0.267	+0.263	1.878	
B. Acetone	As above but C-C-C = 57.3°; 1 methyl eclipsed, 1 methyl staggered	2.95		-0.211	+0.152	1.906	
C. Cyclopropanone	Ref 15, C=O = 1.1906 Å	2.41	2.67 ^b	-0.249	+0.299	1.899	
D. Cyclopropanone	As above but C=O = 1.226 Å	2.63		-0.256	+0.287	1.880	
E. PROPEN	Figures 1a and 1b, C=O = 1.226 ^a and C=C = 1.354 Å ^a	5.13 ^a	5.08 ²⁹	-0.386 ^a	+0.267 ^a	1.639 ^a	1.509 ^a
F. Methyl-PROPEN	Figure 4, C=O = 1.226 and C=C = 1.350 Å	5.24		-0.387	+0.273	1.638	1.528
G. Cyclopropenone	Ref 23, C=O = 1.212 and C=C = 1.302 Å	4.52	4.39 ²³	-0.365	+0.321	1.689	1.707
H. Diphenylcyclopropenone	As above but with 2 phenyls (Figure 4 Ph parameters) in place of H	5.02		-0.362	+0.272	1.681	1.548
I. Dimethylcyclopropenone	As in G, but with 2 methyls (Figure 4 Me parameters) in place of H	4.92		-0.371	+0.288	1.672	1.590

^a Average value from the two molecules. ^b J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968).
^c Total covalent bond order. This is the "bond index" of K. B. Wilberg, *Tetrahedron*, **24**, 1083 (1968).

charge. Using this hypothesis, charge separations of 0.49 e for acetone (from $d_{\text{C=O}} = 1.2122 \text{ \AA}$,¹⁹ $\mu = 2.85 \text{ D}^{28}$) and 0.52 e for diphenylcyclopropenone (from $d = 2.05 \text{ \AA}$, $\mu = 5.08 \text{ D}^{29}$) were calculated.

Additional information on the charge separation magnitudes was obtained from a series of CNDO/2 calculations, a partial summary of which is given in Table X. The charge separation magnitudes, taken as the charge on oxygen q_{O} , are reasonably constant within the saturated ketones, entries A, C, and D, and within the cyclopropenones, entries E-I. The q_{O} in cyclopropanone increases only slightly, 0.007 e, with a 0.035-Å increase in the C=O distance (entries C and D), and the somewhat smaller q_{O} in cyclopropanone (0.249 e in C) compared with acetone (0.267 e in A) is probably associated with the smaller C-C(=O)-C angle in the former. This point is illustrated by the decrease in q_{O} to 0.211 e for an acetone model (entry B) with a 57.3° C-C-C angle. The data for acetone (entry A)³⁰ support Tobey's contention²⁷ that the ketone's dipole moment arises primarily from the carbonyl group, but the magnitude of the charge separation, 0.26-0.27 e, is approximately half the 0.49 e value obtained from a dipole moment based computation.³¹

A very significant result from the Table X data is the 0.12-0.14 e increase in the cyclopropenone q_{O} 's over the q_{O} 's in acetone and cyclopropanone.³²⁻³⁴ This

(28) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955, p 290.

(29) M. A. Battiste, *J. Amer. Chem. Soc.*, **83**, 4101 (1961).

(30) The charge on a methyl C was -0.083 and +0.030, +0.027, and +0.027 for the three methyl H's, giving a total charge of +0.004 e on the methyl group.

(31) The major components of the CNDO/2 dipole moments are: (a) a contribution arising from the atomic charges and their separations; (b) a contribution due to the displacement of charge from the center of the nucleus (polarization of the 2s and 2p orbitals). The atomic charge component of the total calculated acetone dipole moment, 3.03 D (entry A, Table X), is 1.73 D.

(32) The O charge is close to the -0.382 value obtained by D. T. Clark and D. M. J. Lilley (*Chem. Commun.*, 147 (1970)) from an *ab initio* calculation on cyclopropanone. Their bond lengths were C=C = 1.286, C-C = 1.525, C=O = 1.21 Å.

(33) Z. Yoshida and H. Miyahara (*Bull. Chem. Soc. Jap.*, **45**, 1919 (1972)) reported a diphenylcyclopropenone O charge of -0.667 from MO-CI calculations used to investigate the electronic spectrum of the

clearly indicates that charge separation in cyclopropenones is increased by the three-ring unsaturation and that the charge magnitude is not solely a function of the carbonyl group. The effect of the three-ring unsaturation is further illustrated by the C=O bond orders: these parameters are 1.880 and 1.639, respectively, for a cyclopropanone (D) and a cyclopropenone (E) with equal C=O lengths. The q_{O} 's and C=O bond orders for PROPEN (E) and cyclopropenone (G) are similar, but a slight enhancement in charge separation is indicated for the diphenyl derivative. The carbonyl C atom charges (excepting B and G) are reasonably constant from acetone to cyclopropanone to the cyclopropenones, +0.263-0.299. The larger +0.321 value in cyclopropenone (G) itself is undoubtedly due to the inability of the HC=CH moiety to delocalize the amount of positive charge necessary to balance the negative charge on oxygen.

The difference in C=C bond lengths between PROPEN, 1.354 Å, and cyclopropenone, 1.302 Å, is reflected by the C=C bond orders in Table X; compare, for example, the 1.509 for E and the 1.707 for G.³⁵ The bond-order difference is associated with the replacement of hydrogen on the three-ring by phenyl, but it is uncertain that the 0.2 bond-order difference explains

compound. The -0.677 value is too high, as evidenced by the calculated dipole moment of 6.63 D.

(34) A question on the influence of the O...H₂O connection in PROPEN on the intrinsic C=O distance in cyclopropenones was asked by a referee. A CNDO/2 calculation on a methyl-PROPEN...H₂O model ($d_{\text{O...H}} = 2.0 \text{ \AA}$, $\angle \text{C=O...H} = 180^\circ$) gave the following results: $q_{\text{O}} = -0.395$; $q_{\text{C}} = +0.277$; C=O bond order = 1.627. These values differ by -0.008, +0.004, and 0.011 respectively from the unhydrated methyl-PROPEN parameters (F in Table X), and we can therefore be confident that the hydrate influence on the cyclopropenone parameters is minimal. Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, **58**, 334 (1973), reported a similar increase (0.01 e) for the carbonyl O charge in the (CH₃)₂C=O...HOCH₃ system using a modified INDO-CI method. Their O...H distance was 1.784 Å.

(35) The C=C bond order effect was also found in the cyclopropenes. Using Chiang's cyclopropene parameters (C=C = 1.304 Å)^{20b} to define the three-ring structure, the CNDO C=C bond orders were 1.959 for cyclopropene and 1.750 for diphenylcyclopropene. The effect of the C=O group in a cyclopropenone is seen in the 1.750 and 1.548 C=C bond orders for diphenylcyclopropene and entry H and in the 1.959 and 1.707 values for cyclopropene and entry G.

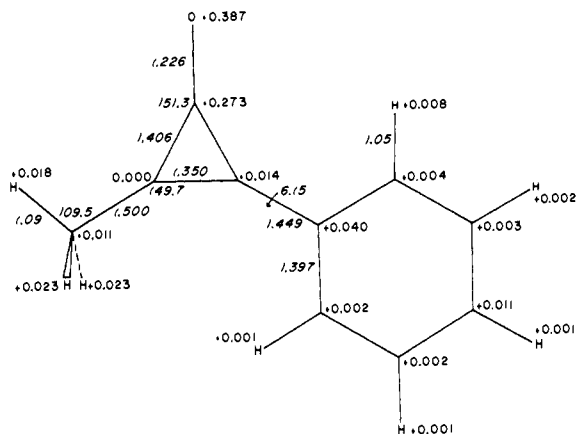


Figure 4. CNDO/2 atomic charges and structural parameters (in italics) for the idealized 2-methyl-3-phenylcyclopropenone model (methyl-PROPEN).

the 0.05-Å bond-length difference. For example, the bond orders in diphenylcyclopropenones E ($C=C = 1.354$ Å) and H ($C=C = 1.302$ Å) differ by only 0.039, and the bond orders in ethylene ($C=C = 1.34$ Å) and stilbene ($C=C = 1.34$ Å) are 2.055 and 1.853, respectively. This matter is under further investigation.

A CNDO-based comparison of the electron withdrawing capabilities of oxygen in PROPEN and dicyanomethylene in CYANOF was made using the 2-methyl-3-phenylcyclopropenone (methyl-PROPEN, F in Table X) and 2-methyl-3-phenyl-4,4-dicyanotriafulvene (methyl-CYANOF) models illustrated in Figures 4 and 5.³⁶ The -0.366 charge in the $C(CN)_2$ portion of methyl-CYANOF is close to the -0.387 on O in methyl-PROPEN, indicating that the electron withdrawing capabilities of O and $C(CN)_2$ are very similar. The two compounds differ, however, in their distributions of + and - charge. The large - charge on O in methyl-PROPEN is balanced by a sizable $+0.273$ on the carbonyl C atom, which is associated with a small total charge of -0.014 on C(2) and C(3). In methyl-CYANOF, however, the total $C(CN)_2$ charge is spread over five atoms, resulting in smaller charges on C(4), -0.112 , and C(1), $+0.123$, and the decrease in the + charge magnitude on C(1) is reflected by a total charge of $+0.067$ on C(2) and C(3). Another way of looking at these data is to consider the net + charge densities on the methyl and phenyl substituents. These values, $+0.128$ for methyl-PROPEN and $+0.175$ for methyl-CYANOF, show that + charge density on the C(2) and C(3) substituents is greater in the dicyanotriafulvene than it is in the cyclopropenone, even though the - charge on O is *ca.* 0.02 e larger than the total - charge on the $C(CN)_2$.

An experimental check of this prediction was provided by Dr. I. Agranat of the Hebrew University of Jerusalem, who synthesized the *p*-fluorophenyl derivative of CYANOF, 2,3-di(*p*-fluorophenyl)-4,4-dicyanotriafulvene, and who recorded the compound's ^{19}F

(36) The methyl-phenyl switch was required in the CYANOF case because the 90 atomic orbitals necessary for a complete calculation exceeded the storage capacity of the CNINDO program. The same 2-methyl-3-phenylcyclopropenylidene coordinates were used for the two models to facilitate comparison of the cyclopropenone and triafulvene moieties. The calculated dipole moment of methyl-CYANOF was 8.88 D ($\mu_{\text{exptl}} = 7.9$ D for CYANOF: E. D. Bergmann and I. Agranat, *J. Amer. Chem. Soc.*, **86**, 3587 (1964)).

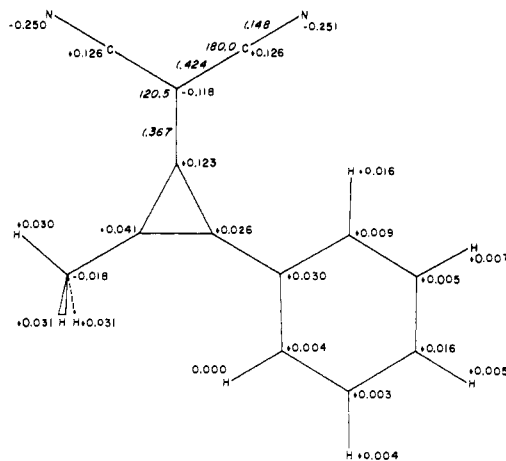


Figure 5. CNDO/2 atomic charges and structural parameters (in italics) for the idealized 2-methyl-3-phenyl-4,4-dicyanotriafulvene model (methyl-CYANOF). The three-ring, and phenyl parameters are the same as in methyl-PROPEN (Figure 4).

nmr spectrum.³⁷ The ^{19}F chemical shifts in *para*-substituted fluorobenzenes supposedly provide a sensitive measure of the σ - and π -electron withdrawing properties of groups *para* to the F atoms.³⁸ This kind of data was used by Tobey in discussing charge separation in cyclopropenones.²⁷ Dr. Agranat's ^{19}F measurements, which were made in CH_2Cl_2 and referenced to external C_6F_6 , gave a 61.5-ppm downfield chemical shift for 2,3-di(*p*-fluorophenyl)cyclopropenone and a 65.5-ppm shift for the CYANOF derivative. The 4.0-ppm downfield shift of the triafulvene relative to the cyclopropenone is in qualitative agreement with the CNDO/2 predictions, indicating a greater electron deficiency in the *p*-fluorobenzene ring of the triafulvene.

Taft³⁸ has published extensively on the use of ^{19}F chemical shifts for the investigation of electron donating and withdrawing effects of groups (X) in *p*-fluoro-substituted benzenes (*p*- FC_6H_4X), including a detailed CNDO/2 study.³⁹ His results have demonstrated an accord between the ^{19}F chemical shifts and several F charge densities and phenyl C charge densities in the vicinity of the F. Similar data for idealized *p*-fluoro models⁴⁰ of methyl-PROPEN and methyl-CYANOF were in qualitative agreement with Taft's results. That is, the various C and F charge densities predicted that the CYANOF ^{19}F chemical shift should appear downfield from the PROPEN value.

The structures of two tetrachloropentatriafulvalenes, **3b** and **3c**, have been determined by single crystal, X-ray analyses.⁴¹ The three-ring and three-ring to five-ring bond distances in these compounds are close to the values found in CYANOF and PROPEN, suggesting that the magnitudes of the charge separation

(37) I. Agranat, private communication.

(38) S. K. Dayal, S. Ekrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 9113 (1972), and references therein.

(39) R. T. C. Brownlee and R. W. Taft, *ibid.*, **92**, 7007 (1970).

(40) The idealized molecular parameters were identical with those used for methyl-PROPEN and methyl-CYANOF but with an added F at a C-F distance of 1.33 Å. The C(4), F, and F 2p, charge densities were respectively $+0.237$, -0.201 , and $+0.049$ in methyl-PROPEN and $+0.243$, -0.197 , and $+0.050$ in methyl-CYANOF.

(41) **3b**: H. Shimanouchi, Y. Sasada, T. Ashida, M. Kakudo, I. Murata, and Y. Kitahara, *Acta Crystallogr., Sect. B*, **25**, 1890 (1969). **3c**: O. Kennard, K. A. Kerr, D. Watson, and J. K. Fawcett, *Proc. Roy. Soc., Ser. A*, **316**, 551 (1970).

in **3b** and **3c** are in the vicinity of 0.4 e. An estimate of the relative capabilities of the O, C(CN)₂, and tetrachlorocyclopentadienyliene groups for — charge stabilization, in PROPEN, CYANOF, and the tetrachloropentatriafulvalenes, can be obtained from the acidities of the conjugate acids H₂O, H₂C(CN)₂, and 1,2,3,4-tetrachlorocyclopentadiene. Although the pK_a of the latter compound is not presently known, the similarities of the pK_a's of water (14) and malononitrile (11.14⁴²), and the similarities between the three-ring bond distance in the cyclopropenone and the three fulvenes, suggest that the pK_a of the tetrachlorocyclopentadiene would be in the 11–14 range. Further attempts to induce even larger amounts of charge separation than the ca. 40% found in CYANOF and PROPEN should consider CH₂X₂ compounds which

(42) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

are substantially more acidic than malononitrile for use as the =CX₂ triafulvene components.

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Supplementary Material Available. Tables IV and VI of the structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-7093.

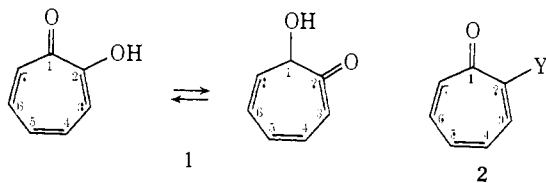
Normal *vs.* Abnormal Nucleophilic Substitutions on Cycloheptatrienones Carrying a Mobile α Substituent. A Rationalization^{1,2}

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Abstract: Reactions of 3,5,7-deuterium-labeled 2-Y-cycloheptatrienones with nucleophilic reactants (N) in DMSO solutions are reported. With N = sodium *p*-tolylmercaptide, C(2) substitution is observed. With N = primary or secondary amines, C(7) substitution is observed when Y = quinuclidinio, while C(2) substitution occurs when Y = Cl or OTs. With N = ammonia, C(7) or C(2) substitution is observed for Y = quinuclidinio or F, respectively, whereas with Y = Cl, substitution at C(7) is accompanied by benzenoid rearrangement. With N = *m*-chloroaniline and Y = Cl, C(2) substitution occurs but the reaction course is diverted to C(7) substitution by added triethylamine. Reaction intermediates are detected spectroscopically. These observations are rationalized in terms of three reversibly interconnected pathways and the synthetic utility is exploited.

Shortly after the first laboratory syntheses of tropolone⁵ (**1**) and tropone (**2**, Y = H),⁶ it was found



(1) (a) "The Reactivity of Pseudoaromatic Compounds. X"; (b) part IX: *Tetrahedron Lett.*, 183 (1973); (c) financial support from Consiglio Nazionale delle Ricerche, Rome.

(2) We thank C. Erkelens, Leiden, for doing deuterium decoupling experiments and Dr. A. J. de Hoog for aid in spectra interpretation.

(3) Postdoctoral Fellow.

(4) Undergraduate.

(5) J. W. Cook, A. R. Gibb, R. A. Raphael, and A. R. Somerville, *Chem. Ind. (London)*, 427 (1950); W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **72**, 2305 (1950); T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, *Proc. Jap. Acad.*, **26**, 38 (1950); *Chem. Abstr.*, **45**, 7098 (1951).

(6) H. J. Dauben and H. J. Ringold, *J. Amer. Chem. Soc.*, **73**, 876 (1951); W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951); T. Nozoe, Y. Kitahara, T. Ando, and S. Masamune, *Proc. Jap. Acad.*, **27**, 415 (1951); *Chem. Abstr.*, **46**, 7558 (1952).

that α substituents on the tropone nucleus, which are stable as anions, can be replaced by a variety of nucleophiles.⁷ However, labeling of the seven-membered ring with isopropyl groups⁸ revealed a complex behavior. Although the nucleophilic reactant was usually found to take the position vacated by Y (the so-called "normal nucleophilic substitution"), with 4- and 5-isopropyl-2-chlorotropone and ethanolic ammonia, 2-amino-5- and 2-amino-4-isopropyltropone were isolated, respectively, in low yields (the so-called "abnormal nucleophilic substitution");⁹ the low yields are due to competing ring contraction of the starting cycloheptatrienone and in many cases, typically with strong bases as reactants, only arene products were observed.¹⁰

This is quite an interesting situation but one which has received very little clarification after more than 20

(7) For a list of such reactions see P. L. Pauson, *Chem. Rev.*, **55**, 9, 56 (1955).

(8) (a) T. Nozoe, *Fortschr. Chem. Org. Naturst.*, **13**, 232 (1956); (b) H. Erdtman and T. Norin, *ibid.*, **24**, 206 (1966).

(9) T. Nozoe, S. Seto, and T. Sato, *Proc. Jap. Acad.*, **30**, 473 (1954).

(10) G. Biggi, A. J. de Hoog, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, **95**, 7108 (1973).